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CHEMISTRY.—*The chemical application of the Raman effect.*[1] JAMES H. HIBBEN, Geophysical Laboratory, Carnegie Institution of Washington.

The Raman effect is too recent a discovery to have what is generally termed a history. It was early in 1928 that Sir C. V. Raman announced his observation of a new type of secondary radiation which was considered as "an optical analogue of the Compton effect." This secondary re-radiation has since been known as the Raman effect.

This subject has been investigated by most of the leading laboratories of the world with the result that within less than a decade there have been considerably more than a thousand publications concerning it. This widespread interest cannot be attributed solely to the novelty of the new discovery, but is primarily due to its fundamental nature from the point of view both of physics and chemistry.

The Raman effect is essentially another parameter by which the behavior of molecules may be measured, independently of their state of aggregation. Other direct methods, such as x-ray and electron diffraction, have indicated the position of the heavier atoms. These methods, like the Raman effect itself, have certain limitations. Fortunately, as compared with the Raman effect, they are complementary in the sense that what one system lacks the other provides. The information obtainable from the standpoint of the Raman method concerns the forces between atoms in a molecule in its normal state, to a certain degree the arrangement in space of the atoms, and their amplitudes and frequencies of vibration. In the simpler molecules this leads to a determination of some of the energy levels the molecules possess. These levels are the warp upon which the pattern of the molecule is woven. Finally this procedure yields in many cases the specific type of chemical linkage which exists in a molecule. This information in turn may lead to the calculation of specific heats and other information of interest to the physicist and to the chemist.

Perhaps the best approach to the problem of what is the Raman effect is to draw an analogy between this and x-ray analysis, which is

[1] Address of retiring President of the Chemical Society of Washington, January 14, 1937. Received February 19, 1937.

known to some extent by everyone. In the latter case the atoms in the given molecule are bombarded with radiation of very short wave length compared to the size of the molecule. The refraction of this radiation may be recorded on the photographic plate as definite spots which are a function of the interatomic distances. In Raman spectra the molecules are bombarded with radiation of longer wave length in equivalent fashion. The type or wave length of light used, however, is in general immaterial. It may be long wave lengths as represented by the red light or it may be short wave lengths as represented by the far ultra violet. In the case of x-rays one deals essentially with a static situation. In the Raman effect it is not static but dynamic.

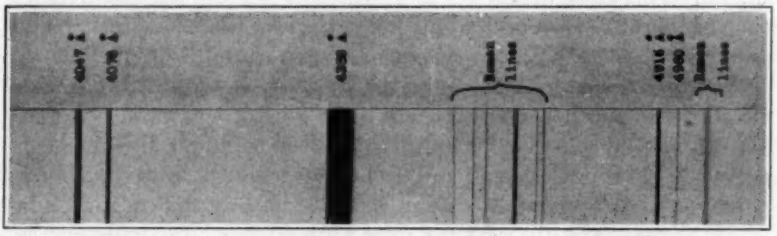


Fig. 1.—Partial Raman spectrum of nitrobenzene showing the 4358Å exciting line.

Here it is a question of the motion of the atoms and the molecule and only indirectly their position in space. Nevertheless, as will be seen shortly, the geometric distribution of atoms does influence the result.

In effect, therefore, molecules, regardless of the state of aggregation, whether they are in the liquid, solid, amorphous or gaseous state, are bombarded with definite light quanta, that is, light preferably of a given single wave length, or what is generally termed monochromatic radiation. When these quanta of energy or photons collide or interact with the molecule, the energy they represent is distributed throughout the molecule in all its vibrational and rotational degrees of freedom. From a spectrographic point of view the results of this interaction are represented, after being transmitted through a spectrograph and photographed on a plate, as definite spectral lines. If real monochromatic radiation is employed (which is very difficult to realize experimentally), then this results in a single line on the photographic plate corresponding to this incident radiation, plus other lines if definite parts of this energy have been subtracted from the original quantum. These lines correspond to different type of vibration and rotation which the atoms in the molecule may possess. The

result is the re-creation or re-radiation of light of longer wave lengths which did not exist in the original light but which is re-emitted by the molecules themselves.

This will be made clearer by means of a diagrammatic illustration of the apparatus used and a picture of these Raman lines as they appear on the photographic plate. These are shown in Figs. 1 and 2.

The source of light illustrated in the first figure is generally a mercury arc. This type of arc has four lines, among many others, which are sufficiently intense and reasonably well separated from other lines to be useful for this purpose. These lines, which do not all appear in

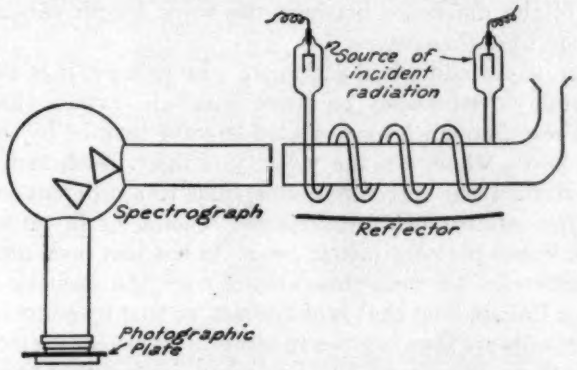


Fig. 2.—Experimental arrangement for recording Raman spectra.

the figure, are at 2537, 4047, 4358, and 5461 Å units. After the selection, therefore, of a given wave length to be employed to excite the Raman lines, the experimental set-up is so arranged that this radiation or light will pass at right angles to the end of the spectrograph through the liquid, gas, or other material to be studied. This is to diminish as much as possible any light, direct from the lamp, which might fall on the opening of the spectrograph, the only desired light being that which comes from the molecules to be investigated. Unfortunately, a spectrograph not only can "see" the light which is reflected, or what is generally termed scattered from the molecules after the interaction, but it can also "see" the light which is scattered from these same molecules in the form of Rayleigh scattering. Neglecting polarization, this is identical with the original exciting radiation. The net result of these two scattering phenomena is therefore a series of lines corresponding to the Raman lines not present in the original light and the more intense line corresponding to the original source of radiation.

The processes thus far described are the essential means used, together with the result obtained. As each of these Raman lines represents a given wave length its position is described on the color scale from the ultra violet to the infra red by this wave length. However, for the sake of convenience in comparing the work of different observers, it is necessary to adopt an additional system to describe these lines. The thing which is of importance is not the wave length per se of the Raman lines, but how much energy has been lost by each photon in giving rise to them. This is the energy which each type of vibration takes up, and consequently the results should be given in terms of the difference between the wave length causing these lines and the lines themselves.

However, as an additional matter of convenience, it is more useful to employ frequencies or wave numbers rather than wave lengths. These frequencies are related to wave lengths by the simple equation, $\lambda\nu = c$, where c is the velocity of light. Each mercury line and each Raman line therefore corresponds to a different value of ν which is the number of vibrations per second, or in terms of the number of waves per centimeter, $\nu = c\bar{\nu}$. As has just been mentioned, it is the difference between the value of $\bar{\nu}$ for the exciting line and the various Raman lines that is of interest, so that by common agreement the results are always given in terms of $\Delta\bar{\nu}$ per centimeter, which represents these differences. The line which is closest to the exciting line in Figure 1, therefore, has the lowest value for $\Delta\bar{\nu}$. These may vary from as low as 60 to possibly as high as 4500.

The simplest type of oscillator is a diatomic molecule. To give rise to a Raman line at all this molecule must have at least one type of atomic motion. The one most frequently encountered for this simple molecule is the linear oscillation of the two atoms in the direction of the valence forces which hold them together. If there is no definite chemical bond of homopolar nature, as in the case of completely ionized molecules, then no Raman line will appear. In the dumb-bell type of molecule, however, where the atoms are held together by a force which may be likened to a spring, the two oscillating components will vibrate with a characteristic frequency. This is true of any mechanical system. In this system the frequency vibration may be calculated from the equation for a harmonic oscillator:

$$\nu = \frac{1}{2\pi}\sqrt{F/m}$$

In an atomic system reducing this to spectrographic terms, $\Delta\bar{\nu} = 4.125 \times \sqrt{F/\mu}$, where F is the valence force in dynes per cm. and μ is the reduced mass as determined by the relative atomic weights. From this it follows that the greatest amplitude of vibration in centimeters of the atoms is given by the following equation:

$$\bar{a} = 8.2 \times 10^{-8} \sqrt{\frac{1}{\mu\Delta\bar{\nu}}}$$

This amplitude varies between 0.06 and 0.09 Å.

For a triatomic molecule there are two possibilities: the molecule may be linear or nonlinear. For the linear molecule there are three possible types of oscillations, the symmetrical, asymmetrical, and deformation oscillation, known as ν_s, ν_a, and δ_s respectively. These give rise to three Raman lines whose frequencies may be calculated. The nonlinear model possesses the types of vibration indicated in Figure 3.

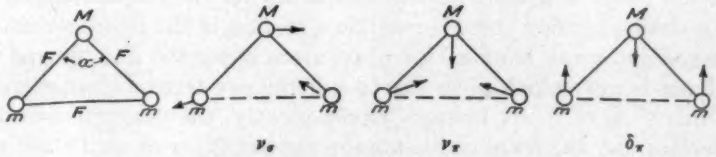


Fig. 3.—The motions of the nonlinear triatomic atom.

In general, in polyatomic molecules composed of several atoms, each atom has three degrees of freedom, so that the total represents 3n degrees of freedom. Of these, three are accounted for by the translational motion and three are described by the rotation of the molecule as a whole about its center of gravity. Consequently there are 3n–6 fundamental modes of vibration and therefore theoretically one Raman line for each mode. This represents a maximum and, as will be seen, is modified considerably by the particular conditions concerning each molecular species. The molecules of the type YX_3 and YX_4, for example, each have four frequencies, and the less symmetrical molecule XY_2Z six frequencies. The symmetry of the molecule occasionally results in one or more frequencies having the same value, the multiple coincidence of frequencies occurring whenever the motions of the atoms performing the vibration are isotropic in several dimensions. When these are isotropic in two or three dimensions respectively they are doubly or triply degenerate.

Each fundamental vibrational frequency in which all the atoms of the molecule participate may correspond to a vibrational Raman line. The relative motions of the atoms in respect to each other, together with the forces exerted between them and their masses, determine the frequency of this vibration or the magnitude of the resulting $\Delta\nu$ shift. Except in the case of a diatomic molecule, it is not entirely accurate to state, therefore, that a particular Raman line corresponds to a single type of linkage such as C–H. However, in any given molecule there is usually some frequency originating in the essential vibration which consists chiefly of the linear or deformation oscillations of atoms of particular groups vibrating in unison. In ethylene, for example, there is one frequency which corresponds to the movement of the two CH_2 groups toward and away from each other. In this case the hydrogen atoms are moving in roughly the same direction as the carbon atoms. As their masses affect but little the C=C vibration, particularly since their motion is in phase with this oscillation, the net result is a characteristic frequency for the ethylenic linkage. In a similar fashion there is possible a motion of the hydrogen atoms toward and away from each carbon atom along the direction of the valence bonds, which gives rise to a frequency termed characteristic of this type of C–H linkage. Consequently, the characteristic frequencies and the force constants for various types of oscillation and bending may be determined. This is particularly valuable, first, because the presence or absence of a type of linkage may thus be possibly established, and second, because these frequencies are slightly altered by the proximity of other groups whose masses or effect on the valence force result in an alteration of the characteristic frequency. This is helpful in the delineation of the molecular structure of the molecule.

Unfortunately, the number of Raman lines which can be elicited from a molecule is not confined to fundamental vibrations, that is, vibrations corresponding to a particular type of motion. Other lines may appear due to overtones (harmonics) of a given frequency or due to combinations. These latter may appear as the sum or difference of other frequencies, the result being in some cases nearly ten times as many lines as are represented by the fundamental vibrations. As a rule, these overtones and combinations have much less intensity than the fundamentals. From this and their numerical values it is sometimes possible, even in a complicated molecule, where a profusion of lines appear in the same neighborhood, to make proper as-

signments. Otherwise it would be very difficult, except in general terms, to state that a given line is due to any particular mode of oscillation. Typical examples of characteristic frequencies and force constants for specific linkage are given in Table 1.

TABLE 1.—VALENCE FORCES (F) FOR DIFFERENT TYPES OF LINKAGE

Linkage	Frequency	$F \times 10^{-5}$ dynes cm^{-1}
C–H*	3050	5.02
C–C	993	4.64
C–O	1030	5.00
C–N	1033	4.85
N–H	3370	6.20
O–H	3650	6.80
H–H	4158	5.05
Cl–H	2880	4.75
Br–H	2558	3.80
S–H	2572	3.78
C–S	650	2.14
C=C	1620	10.60
C=O	1700	11.6
O=O	1556	11.4
C=N	1650	10.40
N=O	1640	11.80
C≡C	2120	15.82
C≡N	2150	17.5
C≡O	2146	18.50
N≡O	2224	20.9

* Aromatic

THE RAMAN EFFECT IN ORGANIC CHEMISTRY

SATURATED ALIPHATIC COMPOUNDS

In general the entire spectrum of the hydrocarbons may be divided into four groups, the first consisting of those frequencies below $\Delta\nu$ 700. These correspond to the deformation or bending motion of the carbon atoms in the chain. From $\Delta\nu$ 700 to approximately 1100 the lines represent the linear or symmetrical vibrations (ν_r) of the carbon atoms and their combination frequencies. From $\Delta\nu$ 1100 to 1470 are deformation (δ_r) oscillations corresponding to the C–H linkage and finally from $\Delta\nu$ 2600 to 3100 the linear (ν_r) oscillations for C–H. The actual magnitude may be illustrated by $\Delta\nu$ 2918 for C–H in methane, 1450 for C–H (δ_r) in the higher homologues and 993 for C–C (ν_r) in ethane. For this region in butane there are no longer single frequencies. The frequencies in the region corresponding to C–H likewise become much more complicated. This is illustrated in Figure 4.

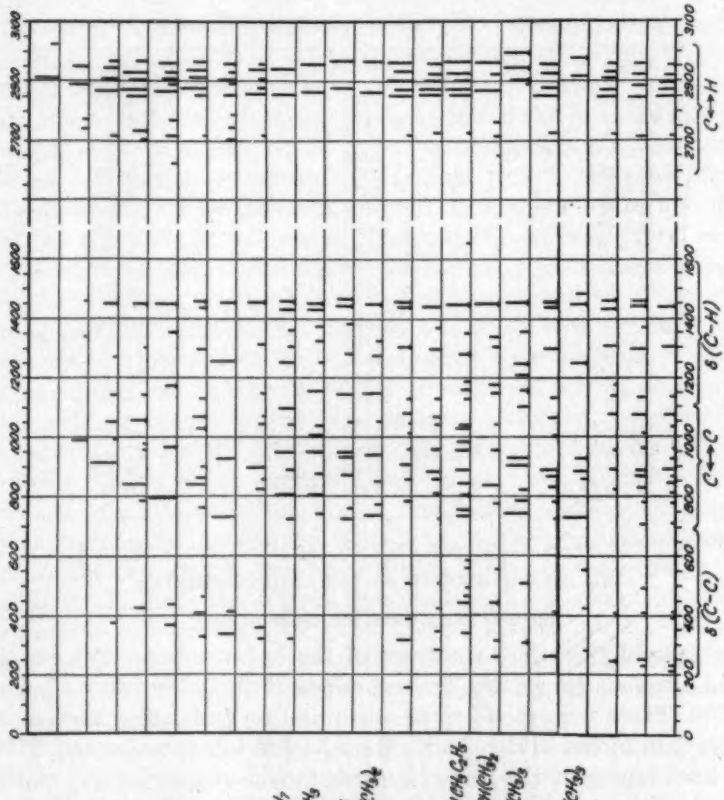


Fig. 4.—Comparison spectra of saturated aliphatic hydrocarbons.

The alcohols show spectra which are quite similar to the spectra of the hydrocarbons with the exception of the frequency occurring near $\Delta\nu$ 3400 which corresponds to the H—O vibration. In no case, however, do any of these compounds give identical spectra.

The ethylene oxides or epoxy compounds are particularly characterized by one or two lines near $\Delta\nu$ 1256 and 1277. In addition there appears a hydrogen frequency greater than $\Delta\nu$ 3000, which occurs only in compounds having a triangular ring structure or in compounds attached to a carbon which is multiply bonded.

The halogen derivatives of the hydrocarbons exhibit characteristic frequencies which are lower than usual, partially owing to the increased mass of the halogen. The ν_r vibrations are $\Delta\nu$ 710, 600 and 530, in methyl chloride, bromide, and iodide respectively. These are not proportional to the square root of the mass and consequently there is likewise progressively a change in the force constant. The effect of halogen substitution on the C—H vibration is to increase its frequency provided the substitution is made on the carbon atom to which is also bound the hydrogen.

Branching of the chains is reflected in altered spectra for all these hydrocarbons.

UNSATURATED ALIPHATIC COMPOUNDS

With very few exceptions the presence or absence of the functional group C=C may be determined by its characteristic frequency shift which occurs between $\Delta\nu$ 1600 and 1680. This is sensitive to groups immediately adjacent, and as it occurs in that portion of the spectrum which is more or less free from other lines, this becomes exceedingly useful in the determination of molecular structure. Ethylene yields $\Delta\nu$ 1620 but propene $\Delta\nu$ 1647. This increase remains constant for all hydrocarbon substituent groups. However, if this group is an aldehyde the frequency becomes $\Delta\nu$ 1618, and if it is a chloride it is reduced still further to 1608. There is likewise an effect on the characteristic C—H frequencies which are two in number, namely, $\Delta\nu$ 3002, and 3080. In vinyl chloride these are augmented to $\Delta\nu$ 3036 and 3134. Two other frequencies appear which remain relatively constant, namely, $\Delta\nu$ 1290 and 1416.

In compounds of the type $CH_3—CH=CHR$ there is introduced another possibility, *cis-* and *trans*-isomerism. As the effect of introducing one radical in place of a hydrogen in proceeding from ethylene to propene was to augment the C=C frequency by twenty wave numbers, the effect of introducing two radicals on each side of the

double bond is to augment the frequency by roughly 40 wave numbers, which gives $\Delta\nu$ 1658 for the hydrocarbon substituents in the *cis*-isomeric form. The *trans*- compounds yield a shift or line 15 wave numbers still higher or $\Delta\nu$ 1674. This again is reduced on the substitution of aldehydes, esters, or acid groups. The results are indicated in Table 2. The trisubstituted ethylenes yield a frequency corresponding in behavior to that of the *trans*- compounds.

TABLE 2.—THE EFFECT OF DISUBSTITUTION ON THE C=C SHIFTS

Radical R	$CH_2=CH-R$	$CH_2-CH=CH-R$		Radical R	$CH_2=CH-R$	$CH_3-CH=CH-R$		
		cis	*trans*			*cis*	*trans*	
CH_3	1647			$CH_3C\equiv CC_6H_5$	1642			
$CH_3O(COCH_3)$	1649	1665	1679	$CHClCH_2$	1640			
CH_2OH	1646	1658	1677	$CH_2C_6H_5$	1640			
$CHOHCH_3$	1646			CH_2Cl	1640		1671	
$CHOHC\equiv CH$	1646		1676	$CHCl_2$			1666	(Kirrmann)
$CHOHCH=CH_2$	1646		1674	$CHBrCH_3$	1635	1651	1666	
C_2H_5	1642	1658	1674	COOH	1638	1645	1652	(Kohlrausch)
C_3H_7	1642	1658	1674	COOR		1644	1655	
C_4H_9	1642	1658	1674	C_6H_5	1631	1642	1665	
C_5H_{11}	1642	1658	1674	H	1620	1647		
C_6H_{13}	1642	1658	1674	CN		1628	1645	(Kohlrausch)
C_7H_{15}	1642			CHO	1618	1625	1642	
$CH(CH_3)_2$		1659	1673	Cl	1608			
				Br	1598			
$CH_2C_6H_5$	1642	1658	1674					
$(CH_3)_2C_6H_{11}$		1657						

A brief example of the use of these shifts to determine the presence of compounds may be cited in mixtures of rhodinol and citronellol which are identical except for the terminal groups. These are respectively:

$$R-CH_2-C(CH_3)=CH_2 \qquad R-CH=C(CH_3)-CH_3$$

The rhodinol, or α-form, yields $\Delta\nu$ 1650 and the β-form 1678.

The effect of conjugation as shown in the diolefins is to reduce the ethylenic frequency very slightly. However, if the conjugation is of the nature found in the allenes, C=C=C, no typical ethylenic shift is observed but instead appear one or two lines occurring at $\Delta\nu$ 1070 and 1130. Allene, like CO_2, is a linear molecule. The nature of this vibration is such as to allow a coupling between the vibrating components in such a way that the usual ethylenic shift is split into two components, one of which occurs at a lower frequency, corresponding to the symmetrical vibration, and one appears at a higher frequency,

corresponding to the asymmetrical vibration. As the latter only appears very weakly in the Raman effect it does not register, the natural result being that the characteristic frequency in this case appears at a much lower value than ordinarily.

CARBONYL COMPOUNDS

Carbonyl compounds, like the ethylenes, yield a double bond shift quite characteristic of the constitution of the molecules. These shifts vary from $\Delta\nu$ 1666 to 1800, depending upon whether the compound is an acid, ketone, aldehyde, ester, or acid chloride, and increase in the order named. The frequency varies slightly on the substitution of different aliphatic radicals in the α-position to the carbon of the carbonyl group; but, as has been indicated, the effect is more pronounced if the substitution takes place directly on the carbonyl carbon. This is likewise shown in a series of esters wherein the frequency remains constant regardless of the ester, but varies widely with the character of substitution on the carbonyl carbon. These effects are indicated in Tables 3 and 4.

TABLE 3.—INFLUENCE OF SUBSTITUTION ON THE CARBONYL FREQUENCIES

Substance	$\Delta\nu$				
	H_3CCOX	RH_2CCOX	R_2HCCOX	R_3CCOX	C_6H_5COX
Acid, X = OH	1666	1652	1648	1644	1647
Methyl ester, X = OCH_3	1736	1735	1732	1728	1720
Ethyl ester, X = OC_2H_5	1736	1732	1728	1724	1721
Ketone, X = CH_3	1710	1709	1709	1702	1677
Acid chloride, X = Cl	1798	1793	1788	1790	
Aldehyde, X = H	1715	1719	1719	1723	1689

TABLE 4.—CARBOYNL FREQUENCY IN ESTERS OF THE TYPE XCOOR

Ester (XCOOR)	$\Delta\nu$						
	X=H	X=Cl	X=CH_3	X=CH_2Br	X=CH_2Cl	X=$CHCl_2$	X=CCl_3
1. R = CH_3	1717	1780	1738	1740	1748	1755	1768
2. R = C_2H_5	1715	1772	1736	1738	1747	1750	1763
3. R = C_3H_7	1719	1775	1739	1736	1742	1749	1764
4. R = C_4H_9	1718	1773	1737	1732	1739	1751	1765
5. R = C_5H_{11}	1718	1774	1738		1744	1756	1769

The remarkable constancy of the carbonyl shift in a series of aldehydes is illustrated in Figure 5, which shows only those shifts below $\Delta\nu$ 1750.

The use of the Raman effect in demonstrating keto-enol tautomerism is illustrated in Figure 6. Here the normal carbonyl frequencies are slightly augmented owing to the effect of conjugation.

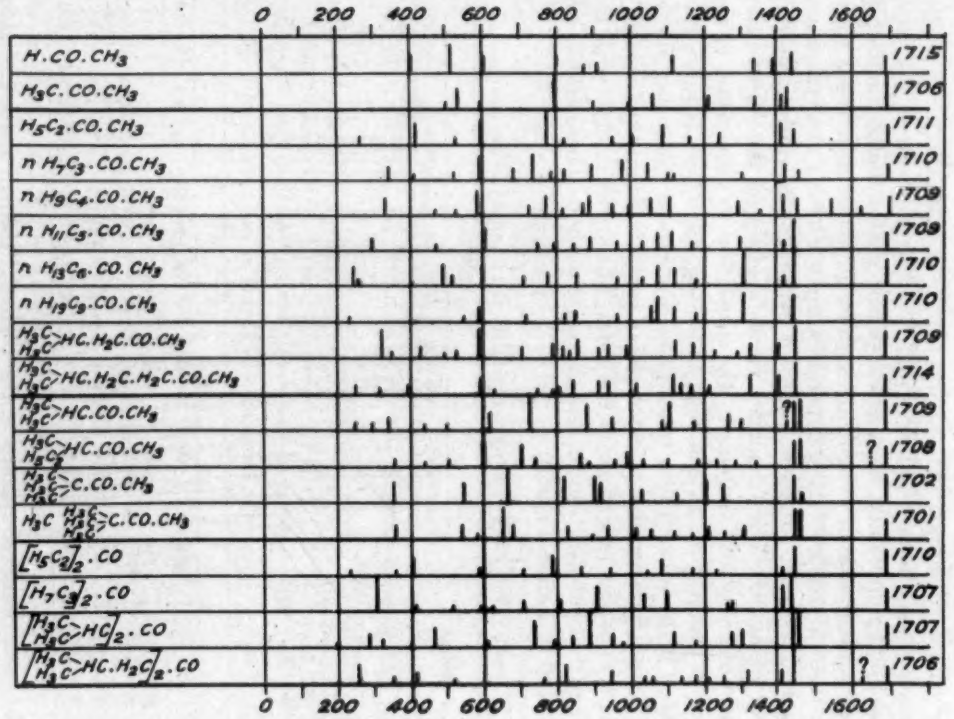


Fig. 5.—The low frequency Raman spectra of aliphatic ketones (after Kohlrausch and Köppl).

From the observations on Raman spectra it has been postulated that diacetyl, acetylacetone, acetonyl, and aldol exist in tautomeric forms.

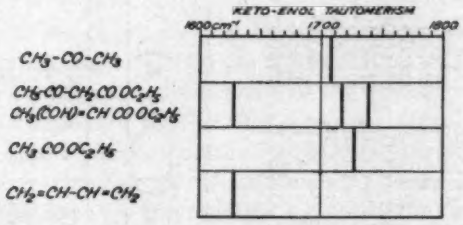


Fig. 6.—The Raman shifts of the keto and enol forms of ethyl acetoacetate as compared with similar compounds (after Andrews).

ACETYLENIC LINKAGE

As is observed in Table I, the force constant for C≡C is approximately three times that obtained for the singly-bonded carbon. The effect of substitution is more pronounced than in the case of the ethylenes but shows the same general behavior. Acetylene yields $\Delta\nu$ 1960. If one hydrogen is substituted by a hydrocarbon radical this increases to $\Delta\nu$ 2120 and remains constant. Disubstitution causes both a marked augmentation of the acetylenic frequency and splitting generally into two components which appear at $\Delta\nu$ 2238 and 2303. The alcohol and ether derivatives sometimes yield three frequencies depending upon the nature of the compound, while on the other hand, halogen derivatives yield but a single line. In addition to this characteristic shift for the acetylenic linkage, there appear in these compounds two others almost equally constant. These are $\Delta\nu$ 340 and 3300. The first of these is probably attributable to the ν_7 vibration of the chain and the second to the ν_1 vibration of the ≡C−H. These effects are illustrated in Table 5.

SATURATED CYCLIC COMPOUNDS

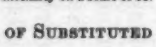
The cyclopropanes are characterized by strong constant frequencies $\Delta\nu$ 860, 1170–1214, and 3065. The last is clearly connected with the hydrogen vibrations, but appears in no other saturated cyclic compound except cyclopropane and its derivatives. The cyclic compounds from cyclopentane to cycloctane show a progressively decreasing frequency in the $\Delta\nu$ 860 region. Otherwise they exhibit remarkable similarity. Nevertheless, it is possible to distinguish the *cis*- and *trans*-isomers in compounds of such types as the cyclohexanes.

TABLE 5.—THE EFFECT OF SUBSTITUTION ON ACETYLENIC FREQUENCIES

$\Delta\nu$

Hydrocarbons								
I		II			III			
$CH \equiv CH$	1960(5)[1]	$CH_3C \equiv CCH_3$	2234(10)		2312(5)	$C_5H_{11}C \equiv CCH_3$	2233(10)	2301(5)
$CH_3C \equiv CH$	2123(7)	$C_2H_5C \equiv CCH_3$	2238(10)		2304(5)	$C_5H_{11}C \equiv CC_2H_5$	2232(8)	2293(5)
$CH_2 = CHC \equiv CH$	2098(7)	$C_3H_7C \equiv CCH_3$	2238(10)		2304(5)	$C_5H_{11}C \equiv CC_3H_7$	2234(7)	2293(5)
$C_4H_9C \equiv CH$	2121(7)	$C_4H_9C \equiv CCH_3$	2235(10)		2303(5)	$C_5H_{11}C \equiv CC_4H_9$	2231(7)	2293(5)
$(CH_3)_2CHCH_2C \equiv CH$	2118(7)	$C_5H_{11}C \equiv CCH_3$	2233(10)		2301(5)	$C_6H_5C \equiv CCH_3$	2214(10)	2253(10)
$C_5H_{11}C \equiv CH$	2118(7)	$C_6H_{13}C \equiv CCH_3$	2233(10)		2303(5)	$C_6H_5C \equiv CC_2H_5$	2210(5)	2238(7)
$C_6H_{13}C \equiv CH$	2119(7)	$C_6H_5C \equiv CCH_3$	2239(10)	2280(1)	2320(1)	$C_6H_5C \equiv CC_3H_7$	2210(2)	2238(7)
$HC \equiv C(CH_2)_6C \equiv CH$	2118(7)	$C_6H_5CH_2C \equiv CCH_3$	2234(10)		2302(5)	$C_6H_{13}C \equiv CCH_3$	2233(10)	2305(5)
$C_6H_5C \equiv CH$	2116(10)	$C_6H_5C \equiv CCH_2$	2214(10)	2253(10)		$C_6H_{13}C \equiv CC_2H_5$	2232(70)	2294(5)
$C_6H_5CH_2C \equiv CH$	2119(10)	$C_6H_{11}C \equiv CCH_3$	2239(10)	2259(2)	2316(2)	$C_6H_{13}C \equiv CC_3H_7$	2233(7)	2294(2)
$C_6H_5C \equiv CH$	2111(10)	$C_6H_{11}CH_2C \equiv CCH_3$	2235(7)		2303(5)	$C_6H_{13}C \equiv CC_4H_9$	2233(7)	2294(2)
$C_6H_5CH_2C \equiv CH$	2120(8)							
$C_6H_{11}C \equiv CH$	2118(7)							
$C_6H_{11}CH_2C \equiv CH$	2118(7)							

[1] The number in parenthesis following the Raman shift in this and other tables represents the intensity on a scale of 10.

TABLE 6.—CHARACTERISTIC FREQUENCIES OF SUBSTITUTED Δ^1-CYCLOPENTENE ()

	R	$\Delta\nu$						
H	899(4)	1025(3)	1207(2)	1296(1)	1441(7)	1467(2)	1615(6)	3060(3)
CH_3	881–903(4)	1026(3)	1207(5)	1295(1)	1439(8)	1465(5)	1658(6)	3045(2)
C_6H_5	890–908(2)	(1033)(10)	1208(6)	1296(4)	1442(6)	1462(1)	1627(8)	(3061)(4)
$CH_2C_6H_5$	887–902(1)	(1030)(10)	1205(2)	1297(3)	1441(7)	1466(2)	1652(8)	3037(3)
CH_2OH	888(8)	1022(2)	1202(6)	1296(3)	1443(8)	1466(3)	1656(8)	3048(4)
CH_2OCOCH_3	889–907(4)	1025(3)	1206(3)	1296(1)	1443(8)	1466(6)	1658(8)	3058(3)
$CHOHCH_3$	893(10)	1026(1)	1207(4)	1294(2)	1444(8)	1468(5)	1651(8)	3051(3)
$CHOHC_2H_5$	895(7)	1029(2)	1206(2)	1294(2)	1441(8)	1464(5)	1650(7)	3052(2)
CH_2Br			1205(2)		1440(7)		1640(7)	
CHO	882(3)		1205(1)	1289(2)	1434(7)		1616(9)	Broad
$COOCH_3$	903(3)	1023(2)	1206(2)	1297(3)	1437(9)	1469(4)	1631(8)	3072(7)
CN	896(7)	1020(2)	1210(3)	1299(3)	1437(9)	1468(4)	1615(8)	3076(8)

CYCLOÖLEFINS

As would be expected, the cycloölefins have a frequency in the region corresponding to an ethylenic group. This is somewhat modified by the ring structure. Appearing at $\Delta\nu$ 1615 in cyclopentene and $\Delta\nu$ 1660 in the Δ^1 substituted derivatives, these compounds also give rise to a frequency near $\Delta\nu$ 3060 characteristic of $=CH_2$. Cyclopentadiene shows a profound modification of the ordinary ethylenic frequency even as modified by the ring structure. This appears at $\Delta\nu$ 1500. The constant frequencies and effect of substitution for cyclopentene and its derivatives are shown in Table 6. The higher homologues such as cyclohexene to cycloheptene give $\Delta\nu$ 1650 for the normal compound, which is augmented to $\Delta\nu$ 1675 by substitution in the Δ^1 position.

AROMATIC HYDROCARBONS

While benzene and its derivatives have been more extensively investigated than any other compounds, their spectra are very complex. Benzene shows the usual $=C-H$ frequency near $\Delta\nu$ 3063 and exhibits $\Delta\nu$ 1605 and 1584. Its derivatives exhibit one frequency for the double bond, namely, $\Delta\nu$ 1600. This is quite appreciably lower than the shift observed in cyclohexene or in ethylene. While the effect of substitution is in the direction of reducing the ordinary ethylenic frequency, this effect is not so pronounced as in the case of cyclopentadiene. Presumably there are 10, or possibly 12, fundamental frequencies, at least one of which has been attributed to a carbon isotope of mass 13.

Attempts have been made to explain the structure of benzene on the basis of resonating bonds. So far as the Raman effect is concerned, the characteristic valence vibration is that of atomic motion along the line of directed valence which varies with the force constant and the mass of the atoms. Where resonance of bonds may be possible, it is the type of bonds which exist for the longest duration of time which determine the spectra. In short, if there is resonance between a double and triple bond, but the bond type is essentially that corresponding to a triple bond, then the Raman shift will occur near the usual position for this type of binding. The concept of resonating bond is based primarily on a change in atomic distances obtained from x-ray data. A conclusion based on this evidence is necessarily an extrapolation. In the case of benzene there is little doubt that the formula commonly used to represent benzene is too static and that there is a continuous resonating effect throughout the ring structure so that no particular atoms can be stated as being doubly bonded.

TABLE 7.—FUNDAMENTAL FREQUENCIES OF BENZENE AND ITS MONOSUBSTITUTION DERIVATIVES

Derivative	$\Delta\bar{\nu}$						
C_6H_6	605(3)	992(10)		1178(3)		1605(1) 1584(3)	3057(1) 3060(5)
a. Hydrocarbon derivatives							
$C_6H_5CH_3$	622(2)	1002(8)	1029(1)	1154(1)	1209(3)	1604(2)	3054(5)
$C_6H_5CH_2CH_3$	620(2)	1003(8)	1029(1)	1157(3)	1203(2)	1604(5)	3052(5)
$C_6H_5CH=CH_2$	623(5)	999(7)	1029(1)	1154(1)	1205(8)	1601(10)	3057(8)
$C_6H_5C\equiv CH$	623(5)	1000(7)	1029(1)	1158(1)	1195(8)	1601(10)	3059(9)
$C_6H_5CH_2CH=CH_2$	623(5)	1000(7)	1029(1)	1158(1)	1205(5)	1599(10)	3057(8)
$C_6H_5CH=CHCH_3$	621(5)	999(8)	1031(1)	1149(5)	1210(8)	1599(10)	3055(8)
$C_6H_5-CH-CH$ $\quad\quad\diagdown\diagup$ $\quad\quad CH_2$	623(5)	999(7)	1026(1)	1156(1)	1220(8)	1604(8)	3061(8)
$C_6H_5-CH_2-C\equiv CH$	623(1)	1000(8)	1033(1)	1158(1)	1200(5)	1601(7)	3059(8)
$C_6H_5C_6H_5$	611(1)	994(5)	1022(2)	1146(1)	1191(1)	1589(3) 1609(5)	3047(8)
$C_6H_5CH_2C_6H_5$	623(4)	1012(8)	1037(4)	1145(2)	1175(4)	1593(6)	3054(4)
$C_6H_5CH_2CH_2C_6H_5$	619(3)	1002(10)	1032(4)	1153(2)	1200(4)	1600(5)	3052(4)
$C_6H_5CH=CHC_6H_5$ (*trans*)	620(3)	1004(10)			1188(15)	1590(15)	
$C_6H_5CH=CHC_6H_5$ (*cis*)	615(2)	1000(10)	1027(2)	1150(4)	1190(4)	1596(10)	3059(4)
$C_6H_5C\equiv C_6H_5$	621(2)	997(15)	1028(1)	1140(15) 1155(2)	1174(2) 1188(2)	1590(20)	
b. Benzyl compounds							
$C_6H_5CH_2Cl$	619(4)	1000(3)	1034(1)	1159(1)	1211(1)	1600(1)	3054(3)
$C_6H_5NH_2NH_2$	622(4)	1001(8)	1028(2)	1156(4)	1201(4)	1606(4)	3055(8)
$C_6H_5CH_2OH$	610(0)	1000(3)			1196(1)	1594(2)	3050(3)
$C_6H_5CH_2NO_2$	623(4)	1005(8)	1029(3)	1160(2)	1197(3)	1596(5)	3059(4)
$C_6H_5CH_2CN$	620(2)	1007(4)	1030(1)		1187(2)	1597(2)	3057(4)

Nevertheless, it is precarious to consider that the average effect is a bond and a half. The Raman frequency would seem to indicate that in view of the modifications of the ethylenic frequency by ring structure in cyclopentene, in benzene there are double bonds with a slightly diminished force constant.

The effect of multiple substitution in benzene is to decrease the C = C shift with increasing substitution, but no two isomers are identical. The more or less constant frequencies observed in benzene and some of its derivatives are indicated in Table 7.

TERPENES, TERPENE DERIVATIVES, AND TERPINOIDS

The structure of these compounds may be extraordinarily complex. Particularly has it been difficult to differentiate the components of the various mixtures occurring in natural products. From a spectrographic standpoint, however, it has been shown that most of these mixtures contain some type of bonding which permits the determination of types of compounds in distillates and, in particular cases, their structures. Limonene has an external double bond which correctly falls in the neighborhood of $\Delta\nu$ 1650, while the internal double bond $\Delta\nu$ 1681 is similar to methyl cyclohexene. The compound *dl*-$\Delta\Delta^4$-carene gives $\Delta\nu$ 1554, 1639, and 1670, as compared with 1641 and 1683 for *d*-Δ^3-carene. The *l*-Δ^3-carene has only $\Delta\nu$ 1685. The sabinenes, on the other hand, give $\Delta\nu$ 1653. Geranial and citronellal show very different shifts, as likewise do citronellol and linaloöl. Some of these differences are indicated in Figure 7.

Those compounds possessing a $=CH_2$ group, or equivalent, yield the C—H frequency characteristic of this type of binding. From carvone and limonene are observed $\Delta\nu$ 3034 to 3085. Pulegone correctly exhibits no such frequency. The appearance of this higher frequency shift in these compounds is in contradistinction to the behavior of the substituted cyclohexenes.

Some examples of the use of Raman spectra are found in the analysis of many complicated mixtures of terpenes, and the indication of the existence of anethole, isoeugenol, and isosafrole as the *trans*- rather than the *cis*-compounds.

This is only a casual indication of the many applications of constitutional determination by means of the Raman effect to the delineation of the structure of the terpene derivatives. These are of great interest in the biochemical fields embracing vitamins, hormones, and compounds of biological significance.

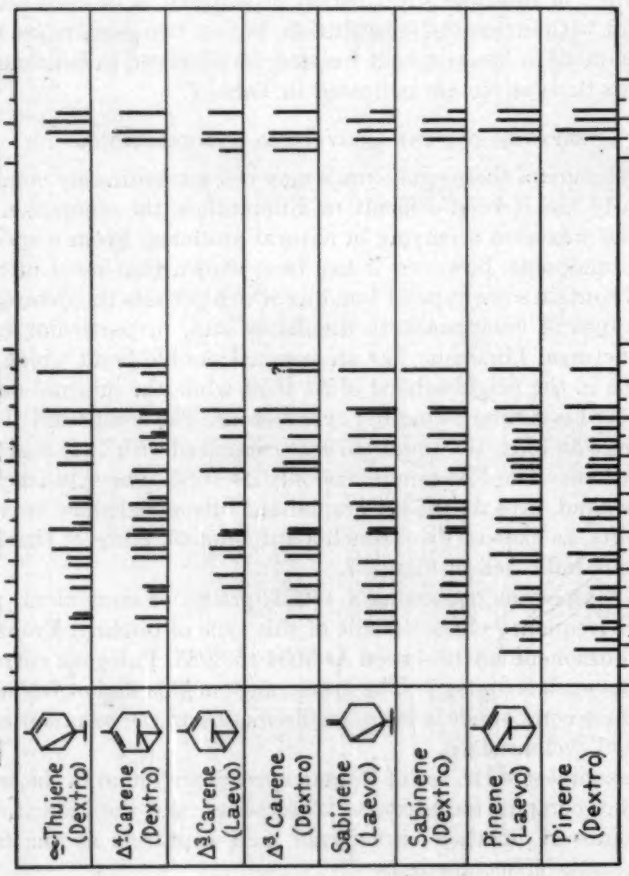


Fig. 7.—The Raman spectra of some polycyclic terpenes (after Nevgi and Jatkar).

POLYCYCLIC COMPOUNDS AND DIPHENYL DERIVATIVES

These compounds exhibit spectra of the expected kind in view of the tenets thus far promulgated. Some lines alter widely with substitution and others remain relatively constant. The ethylenic shift is slightly less than $\Delta\nu$ 1600 in most cases.

ALIPHATIC ORGANIC SULFUR AND METALLO COMPOUNDS AND THOSE CONTAINING NITROGEN

The H—S linkage is as characteristic as any other so far described. It occurs at $\Delta\nu$ 2573 in both organic and inorganic compounds. The C—S line appears at $\Delta\nu$ 652, with the exception of methyl mercaptan which gives $\Delta\nu$ 704. The determination of S—S in the polysulfides is not entirely satisfactory and the assignment of a particular frequency to a characteristic vibration is not without objection. Presumably this occurs at $\Delta\nu$ 510. All the polysulfides and sulfides are easily distinguished from other types of compounds.

The N=O frequency appears at about $\Delta\nu$ 1565 in the nitrites, and 1640 in the nitro compounds and nitrates. The C=N line appears at $\Delta\nu$ 1650 as determined primarily from the oximes. The methyl derivatives of these compounds are the only ones showing a hydrogen frequency in excess of $\Delta\nu$ 3000 for this type of compound.

The isonitriles exhibit two frequencies which appear in the triple-bond region, namely, $\Delta\nu$ 2146 and 2161. The nitriles, on the other hand, exhibit a frequency which is approximately 100 wave numbers higher. The thiocyanates and isothiocyanates yield frequencies which occur within a relatively narrow range of $\Delta\nu$ 2106 to 2182. The isothiocyanates, however, exhibit two frequencies like isonitriles. These compounds also give rise to a line near $\Delta\nu$ 630 which has been pointed out as possibly characteristic of the C—S linkage.

Metallo derivatives such as zinc or mercury dimethl and tetraethyl lead have their principal frequencies at less than $\Delta\nu$ 700. Those in excess of this amount are connected with the methyl radicals. There are usually about four frequencies concerned with the metal atom to carbon vibrations, which vary from $\Delta\nu$ 130 to 700. There is no similarity in the frequency shifts in this region between any of these compounds.

The amines, amides, and imido compounds are characterized primarily by the hydrogen shifts which occur from $\Delta\nu$ 3319 to 3378 in the aliphatic compounds and from $\Delta\nu$ 3360 to 3420 in the aromatic ones. The C—N shift as determined for methyl amine occurs at $\Delta\nu$ 1033. The carbonyl frequency in the amides is greatly reduced from

the corresponding frequency in the ketones and appears at 1600 in lieu of 1710.

HETEROCYCLIC COMPOUNDS

The unsubstituted furanes, pyrroles, and thiophenes exhibit an anomaly somewhat similar to those observed in cyclopentene. There is no C=C shift in the normal position, but one occurs at $\Delta\nu$ 1486 in furane, possibly at 1140 in pyrrole, and 1404 in thiophene as compared with 1500 in cyclopentadiene. The substitution of a radical in place of a ring hydrogen immediately causes the appearance of a reasonably normal ethylenic shift if due allowance is made for ring influence. The normal C=N frequency is also lacking in 3, 4-dimethyl furazan. Unfortunately, furazan has not been studied. The remaining furazans investigated, azoximes and oxdiazoles have at least one C=N shift. This group of compounds is also characterized by C−H lines from $\Delta\nu$ 3070 to 3349 in some cases. The intercomparison between the spectra obtainable from some of these compounds is given in Table 8. The pyrroles give rise to approximately $\Delta\nu$ 3140 in all cases, but, in addition, to 3380 when there is a hydrogen attached to a nitrogen atom.

TABLE 8.—THE RAMAN SPECTRA OF SOME FURAZANS, OXDIAZOLES, AND AZOXIMES

3, 4-Dimethyl furazan	2, 5-Dimethyl-oxdiazole	3-Methyl-4-phenylfurazan	2-Methyl-5-phenyloxdiazole	5-Methyl-3-phenylazoxime	3-Methyl-5-phenylazoxime
289(1)		283(1)			
649(1)	613(1)	621(1)	629(1)	635(1)	632(2)
709(2)					958(1)
964(1)	923(1)	998(2)	991(1)	989(2)	982(1)
	1043(1)		1030(2)	1020(1)	1036(2)
				1055(1)	1069(1)
	1108(2)		1102(2)		
		1168(2)	1175(2)		1183(2)
1308(2)		1278(1)		1305(2)	1320(1)
1396(3)					
1461(3)	1438(3)	1451(3)	1442(2)	1439(2)	1463(2)
		1502(2)	1482(3)	1483(2)	1499(2)
		1546(3)	1546(3)	1541(3)	1559(3)
	1579(3)	1598(3)	1591(2)	1576(2)	1601(2)
2938(2)	2957(2)	2936(2)	2919(2)	2928(2)	2940(1)
3070(1)	3082(1)	3083(2)	3071(2)	3065(2)	3091(2)
		3190(1)	3182(1)	3178(1)	
3217(1)					3204(1)
	3349(1)				

DEUTERIUM COMPOUNDS

If mass alone enters into the ratio of the frequency observed for deuterium to that of hydrogen it is as $1:\sqrt{2}$ or $\Delta\nu_D = \Delta\nu_H \, 1/\sqrt{2} = 0.707 \times \Delta\nu_H$. For CD_4 is observed 2108, compared with 2915 in CH_4. CD_4

should give a calculated value of 2065. In $CHCl_3$ there are two frequencies whose counterparts in $CDCl_3$ are very different. These are $\Delta\nu$ 1215 and 3019. In $CDCl_3$ these become $\Delta\nu$ 908 and 2256, as compared with a calculated value from mass effect alone of 860 and 2140. Consequently, the observed frequency is higher than the mass effect allows, indicating an increased force of linkage in the deuterium compounds. Deuterium derivatives have a special usefulness in the assignment of doubtful vibrations. It will be remembered that in the region between $\Delta\nu$ 1000 and 1400 there occur many lines whose origin is unknown. If these lines are due to the atomic vibrations of carbon as the principal participant, then these will be altered only slightly by the substitution of deuterium for hydrogen. On the other hand, if the lines correspond to a frequency chiefly concerned with the motion of the hydrogen atoms, then the substitution of deuterium will cause a profound modification of the frequencies as is indicated in the examples just given.

SOME APPLICATIONS OF THE RAMAN EFFECT TO ORGANIC CHEMISTRY

Thus far have been outlined the nature of the Raman effect, and the mechanism by which the observed Raman spectra may be used to delineate the structure of organic molecules. It has been indicated that in the simpler molecules the modes of vibration of the atoms can be determined, as well as their spacial configuration, their amplitudes of vibration, the forces involved in types of linkage, and the specific heats if all the types of vibration are known; and finally much light can be thrown upon the constitution of molecules by characteristic Raman shifts.

Since the known constitution of molecules should give rise to certain types of Raman spectra, it is possible to distinguish alterations of this constitution under different conditions. For example, no one has ever isolated methylene glycol, and yet an aqueous solution of formaldehyde indicates that formaldehyde continues to exist no longer and is converted to methylene glycol. The mechanism of the polymerization of polystyrene and acetaldehyde is demonstrable, and organic and inorganic complexes can be investigated by the change in spectra. These applications are of particular interest in the field of industrial plastics.

The number of molecules in higher vibrational levels at room temperature can be determined, in some cases, by the intensities of anti-Stokes lines. These are like ordinary Raman lines except for the fact that they are emitted by molecules already in a higher energy state

than the ground level and consequently appear on the high frequency side of the exciting line rather than the low frequency side. In addition to the magnitude of frequency shifts and their intensities, there exists a third property of Raman spectra which is helpful in the assignment of different frequencies to their proper origin, and consequently in the determination of the types of vibration the molecules undergo. This is the measurement of the degree of depolarization of any given Raman line. Those lines corresponding to symmetrical oscillations are more or less polarized, while those which are unsymmetrical will be depolarized to a greater or less degree, depending on the character of the oscillation.

All the principles thus far set forth are equally applicable to inorganic chemistry.

THE RAMAN EFFECT IN INORGANIC CHEMISTRY

Ordinarily inorganic chemistry has been little concerned with interatomic forces or spacial configurations, and has been more or less content with classical formulae and percent composition of the elements. For the average practical purpose this is sufficient, but if one is interested in surface tension, vapor pressure, osmotic pressure, viscosity, and other factors for which the behavior and configuration of the molecules as well as the chemical composition are important, then the Raman-spectra method will give information of value. A perusal of any standard reference book in inorganic chemistry will readily convince the skeptic that in spite of the free use of simple formulae, there is a large field of inorganic chemistry concerning which there exists a most profound state of ignorance.

The inorganic groups have characteristic frequency shifts just the same as the organic ones and for the same reason. There is, however, a larger scale of diffuseness or lack of clarity which is attributable to a much wider scale of binding, ranging from the completely homopolar type found in organic chemistry to the completely heteropolar type which may exist in inorganic compounds. The latter type gives rise to no Raman lines. Hydrochloric acid solutions, for example, give no frequency shift, but HCl yields $\Delta\nu$ 2880 in the gas and somewhat less in the liquid.

As is to be expected, crystals, liquids, solutions or gases yield shifts depending on the binding forces and on the spacial arrangement of the atoms, that is, tetrahedral, triangular, linear, etc. All ions or molecules of the type RO_4 or RO_3, etc. have their respective shifts somewhat similarly spaced. The number of lines and the exact magnitude, how-

ever, depend on the mass, force, and other considerations named.

The shifts observed in the SO_4 group, while characteristic of that group, are not wholly independent of the cation. The frequency near $\Delta\nu$ 1000 decreases regularly with different cations in a given periodic group directly proportional to the mass of the cation. The difference is not more than 20 wave numbers.

The nitrites yield several lines the principal of which is $\Delta\nu$ 1325, a symmetrical vibration. The nitrates give $\Delta\nu$ 720, 1048, 1357, wherein 1048 is the symmetrical vibration. Sulfates yield $\Delta\nu$ 440, 620, 984, and 1104. A comparison of the spectra of the various nitrates and sulfates is given in Tables 9 and 10.

All inorganic compounds (possessing at least a weak homopolar linkage) likewise exhibit entirely different spectra, depending on the atomic constituents, and it would serve no useful purpose to enumerate all of them. The method used to delineate structure in inorganic chemistry from the point of view of the Raman effect is the same, in principle, as that employed with organic compounds. A few of many possible examples will be given to illustrate some of the results obtained respectively in solution, from solids, gases, acids, and finally from that most peculiar of all compounds, water itself.

It has been more or less customary to consider a solution of SO_2 in water as sulfurous acid. While there no doubt is some H_2SO_4 present under these circumstances, in the main, this is principally SO_2 in water, as the spectrum of gaseous SO_2 is practically unaltered on solution. Similarly it can be shown that the anions of the compounds $NaHSO_3$ and $K_2S_2O_7$, in solution exist primarily as $S_2O_5^-$ and $KHSO_4$ respectively. The compound $TiCl_4$ in strong HCl solutions indicates the existence of H_2TiCl_6. The complex ammonium, cyanide, tungsten, and molybdenum compounds have particular frequencies.

In liquids it can be demonstrated that there are mixed compounds formed on addition of PCl_3 to varying quantities of PBr_3, while in the solid state the Raman spectrum from the solid eutectic of $NaNO_3 + KNO_3$ shows a single sharp frequency for the NO_3 group when freshly prepared, but reverts to two separate shifts after a period of several days. The polymerization of silica in glasses can be shown. The polymerization of gaseous SO_3 and the depolymerization of S_2O_6 can be quantitatively demonstrated since the spectra of the two compounds are quite distinct. Concentrated H_2SO_4 gives a spectrum which is quite different from that of dilute solutions of this acid. There are three lines, $\Delta\nu$ 1048 characteristic of the HSO_4^- ion, 982 for the SO_4^- ion and 908 probably for the un-ionized H_2SO_4 molecule.

TABLE 9.—RAMAN SPECTRA OF SOME SULFATES

Substance	Concentration	Raman shifts								
Li_2SO_4	18 per cent	442	593		984(10)	1110(5)				
Na_2SO_4	Saturated	460(5)	615		981(10)	1101				
K_2SO_4	Saturated	457(5)	619		981(10)	1090				
$(NH_4)_2SO_4$		454(5)	618		982(10)	1107	1285(2)		1467	
$K_2Al_2(SO_4)_4$		477	607	(790)[1]	977(5)	(1160)				
$CuSO_4$		279? 429	610(5)	717–754	980(10)	(1058	1110	1143)	1472	1665
$MgSO_4$		456(5)	617	(706)	982(10)	1116				
$BeSO_4$		442(5)	613		980(10)					
$ZnSO_4$		454(5)	620		982(10)	1106				
$CdSO_4$		451(5)	621		983(10)	1108				
$Al_2(SO_4)_3$		457(5)	614		980(10)	1104				
$MnSO_4$	1 *N*	452(5)	613		988(10)					
$FeSO_4$	3 *M*, Saturated	(381)	673		978(5)					
$NiSO_4$					980(10)					

[1] When the Raman shift is given in parenthesis it indicates a doubt as to the reality of the observation.

TABLE 10.—RAMAN SPECTRA OF SOME NITRATES

Substance	Concentration	Raman shifts									
$LiNO_3$	14 *N*					1050(10)					
$NaNO_3$	33 per cent			721(2)		1049(10)	1361(2)	(1389)	1414	1663[1]	
KNO_3	Saturated (20 per cent)			730(2)		1049(10)	1357(2)		1413	1659	
$RbNO_3$	20 per cent					1048(10)					
$CsNO_3$	20 per cent					1046(10)					
NH_4NO_3	64 per cent				728(2)	1050(10)	1332(2)	1361	1400	1659	
$Cu(NO_3)_2$		279	442	717(5)–754(2)		1048(10)	1325(2)–	1421	1476	1654	
$AgNO_3$						1041(10)					
$Be(NO_3)_2$	3 *N*					1049(10)					
$CdNO_3$	8 *N*			716(2)	741(2)	1047(10)					
$Mg(NO_3)_2$	3 *N*	(376)				1049(10)	1346	–1427		(1655)	(1811)
$Ca(NO_3)_2$	Saturated		721	716(2)–741(5)		1050(10)	1349	–1441		1647	(1811)
$Sr(NO_3)_2$	Saturated			728(2)		1049(10)	1354(2)				
$Ba(NO_3)_2$	Saturated			720(2)		1049(10)	1350(2)				
$Zn(NO_3)_2$	3 *N*					1047(10)					
$Al(NO_3)_3$	3 *N*					1049(10)					
$Pb(NO_3)_2$	Saturated			730(2)		1047(10)					
$Bi(NO_3)_3$				730(2)	980	1036(10)	(1236)	1417(2)			

[1] The Raman shifts indicated in this column are due to the water present.

The intensity of these three lines varies with dilution. This is demonstrated in Figure 8. While NaHS exhibits an S—H line, neither H_3PO_4 nor H_2SO_4 shows any linkage between the phosphorus or sulfur and the hydrogen atoms.

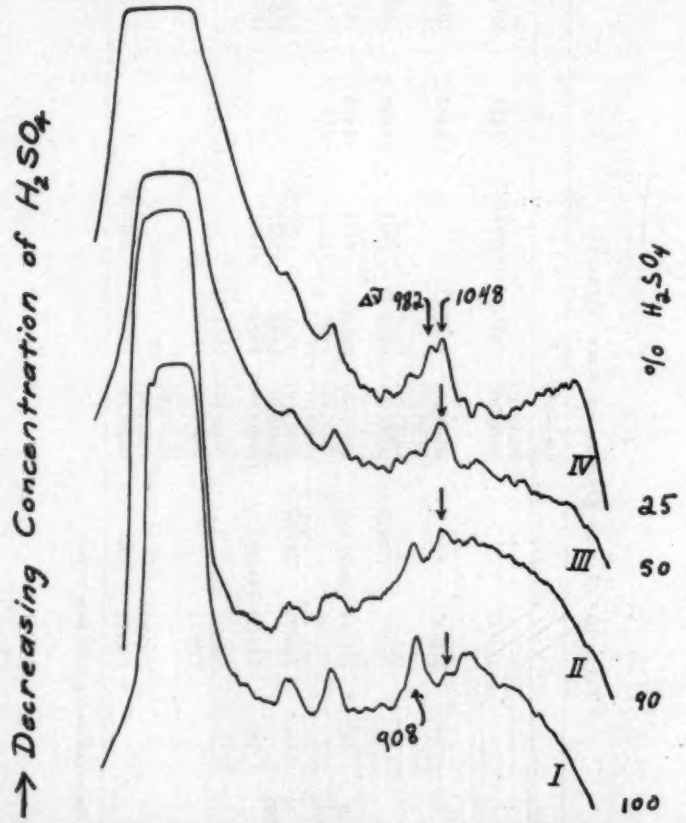


Fig. 8.—Changes in the characteristic Raman frequencies of sulfuric acid with varying concentrations. $\Delta\bar{\nu}$ 908 characteristic of sulfuric acid molecule decreases in intensity with dilution; $\Delta\bar{\nu}$ 1048 characteristic of HSO_4 ion, and $\Delta\bar{\nu}$ 982 characteristic of SO_4 ion increases in intensity with dilution (after Woodward).

Nitric acid also possesses different lines at varying concentrations. In dilute solution there is $\Delta\bar{\nu}$ 1046 for the NO_3^- ion which appears only very weakly, if at all, in the concentrated acid. On the other hand, as the acid becomes more concentrated there appear two frequencies $\Delta\bar{\nu}$ 1300 and 1665. These are more or less analogous to the

similar frequencies appearing in CH_3-O-NO_2, and give some evidence of the existence of the ester form of nitric acid in concentrated solution. These changes are indicated in Figure 9. Stepwise dissociation is also shown from the spectra of selenious and selenic acid as well as for phosphoric acid.

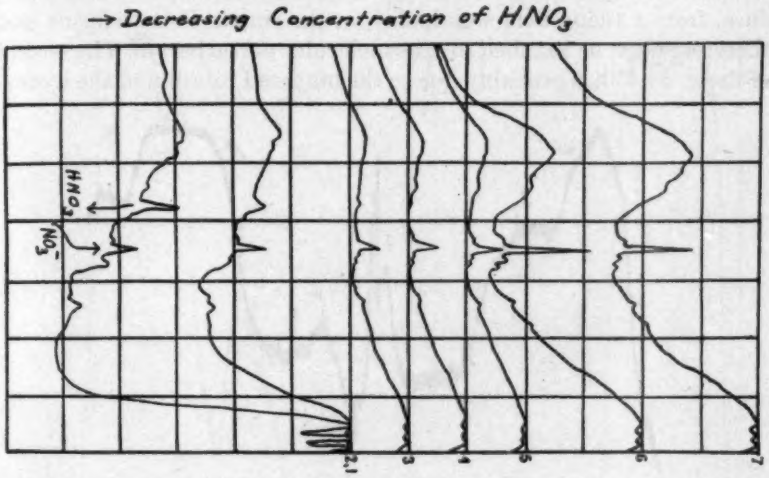


Fig. 9.—Changes in the characteristic Raman frequencies of nitric acid with varying concentration. Showing increase in nitrate ions and decrease in nitric acid molecules with dilution (after Rao).

Perhaps one of the more interesting applications of the Raman effect in inorganic chemistry is in the investigation of the constitution of water. The anomalous behavior of water from the physicochemical point of view has long been ascribed to various types of polymers. The explanations have varied from postulating the existence of $(H_2O)_2$ and $(H_2O)_3$ to the assumption of a quasi-crystalline arrangement having respectively a tridymite, quartz, and close-packed ideal structure. It has been postulated that these modifications change as a function of temperature. The difference between these concepts is more illusory than real. The essential fact is that there is a profound influence on the Raman spectrum of water as changes in its constitution take place. This is prima facie evidence of the existence of the intermolecular interaction in water. Other methods of arriving at this conclusion are less direct and more susceptible to error. Water may have theoretically but three fundamental frequencies. These occur near $\Delta\nu$ 1600 (δ_τ), 3600 (ν_τ) and 3757 (ν_s) from the vapor. In the liquid

the second of these three is lowered and split into three components. The last one, observable in infra-red absorption, is forbidden in the Raman effect. The Raman spectrum of water, however, has three other broad frequencies, namely, at approximately $\Delta\nu$ 150, 450, and 2118. Of these $\Delta\nu$ 2118 is probably a combination of the frequencies $\Delta\nu$ 1630 and 450. This leaves the $\Delta\nu$ 150 and 450 as impossible of existence, from a theoretical standpoint, in the simple H_2O molecule and therefore must be ascribed to intermolecular perturbation. The second of these, $\Delta\nu$ 450, is probably due to the hindered rotation of the hydro-

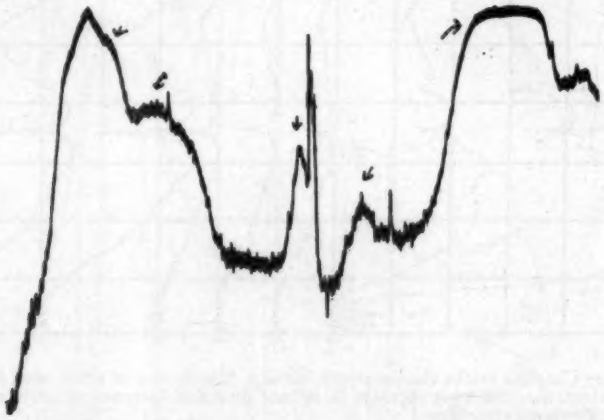


Fig. 10.—A microphotometer tracing of the principal Raman bands for water excited by the 2537 Å mercury line. The bands are indicated by arrows from left to right to correspond to $\Delta\nu$ 150, 445, 1628, 2170 and the broad band extending from $\Delta\nu$ 3220 to 3600.

gen atoms in a given molecule, and the first to the hindered translational motion of the molecules as a whole. Both of these effects are therefore directly attributable to the influence of one molecule on the other and constitute a phenomenon unique in Raman spectra unless there is a close chemical or physical combination. The assignment of vibrational and rotational motion to these two frequencies is further substantiated by the spectrum from deuterium oxide. In this compound the $\Delta\nu$ 450 for hydrogen rotation is diminished, but $\Delta\nu$ 150 is little affected.

A microphotometer tracing of the Raman spectrum of water is shown in Figure 10. Instead of reasonably sharp lines there are observed broad bands due to the lack of specific quantitization in the energy changes. The values given for the shifts represent the peaks of the bands. It may be pointed out that the maxima of the broad

bands between $\Delta\nu$ 3200 and 3600 change somewhat with temperature, and, as may be expected, the two lower frequencies, $\Delta\nu$ 140 and 450, diminish markedly with an increased temperature. As ice is supposed to be polymerized, one would expect an increase in the intensity of the lower frequencies accompanying a change in state from water to ice. This is indeed the case, as is shown in Figure 11.

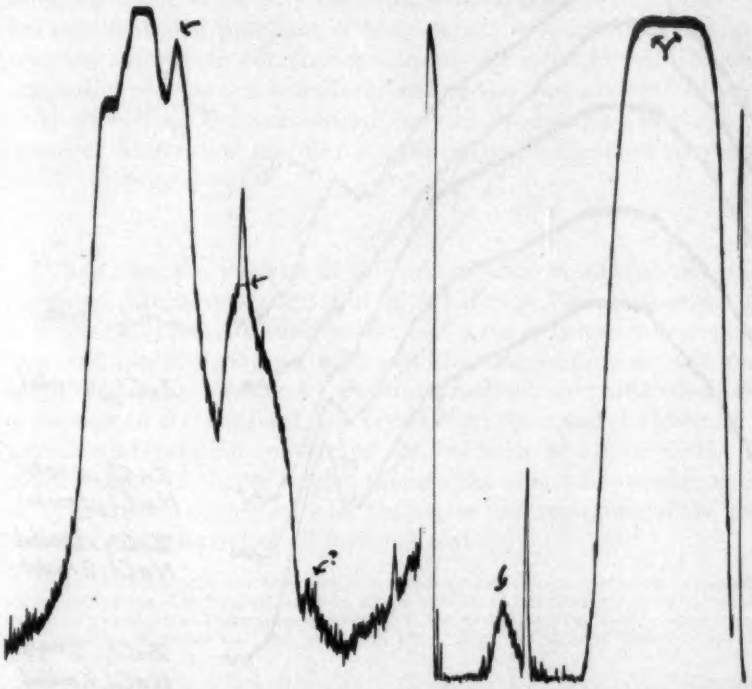


Fig. 11.—A microphotometer tracing of the Raman spectrum of ice showing the enhancement in intensity of the lower frequency shifts occurring in ice at $\Delta\nu$ 205 and 601 as a result of intermolecular interaction.

Another interesting application from the point of view of inorganic chemistry is the demonstration of the common ion effect. This is shown in Figure 12. Zinc chloride has at least one strong line at $\Delta\nu$ 280. The top curve in the figure represents a one-molal solution which shows the zinc chloride line with fair intensity. On further dilution the line practically disappears, indicating an increase in ionization which is more rapid than the corresponding dilution. However, as is shown in the lower curves, the addition of the common chloride ion by means of NaCl causes a suppression of this ionization, so that

the actual concentration of un-ionized zinc chloride is greater in the half-molal $ZnCl_2$ solution under these circumstances than it was originally in the one-molal solution.

These examples will suffice to demonstrate that the constitution of inorganic as well as organic compounds can be determined in many

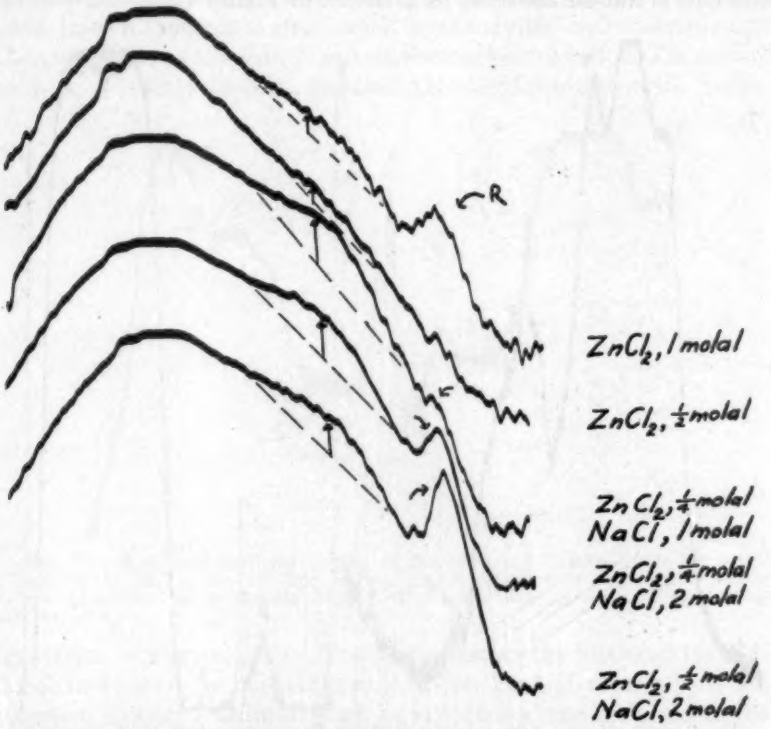


Fig. 12.—An enlarged microphotometer tracing of zinc chloride and zinc chloride-sodium chloride solutions showing the common ion effect which results in the repression of ionization in zinc chloride.

cases. This is of particular interest in those examples where there is either a change in passing from a pure compound to solution or where there is an alteration in composition or constitution induced by any modification of environment.

All the general types of Raman spectra investigations enumerated in the course of this presentation have been undertaken in the Geophysical Laboratory. This work has included a study of many organic and inorganic compounds from a structural standpoint, those com-

pounds which exhibit peculiarities such as oxalic acid and formaldehyde solutions, and finally the mechanism of polymerization and association. It has been assumed that any method which will not yield logical results in the field of organic chemistry is inapplicable to the investigation of properties of inorganic compounds which are, in turn, more directly concerned with geophysics. Most of the common inorganic salts, bases and acids have been examined and the results applied to the constitutional problems of these substances, in solution, and as crystals, amorphous compounds and inorganic complexes. The demonstration of common ion effects and of the "association" of water and ice has likewise been realized. In brief, fundamental physical and chemical information has been obtained concerning those substances which compose the earth.

SUMMARY

It has been the purpose of this presentation to outline the interpretation, the development and application of Raman spectra and, to a certain extent, to analyze the data upon which such interpretations and applications are predicated. The contributions already made to physics and chemistry by the Raman effect are undisputed. It is of interest to the physicist, the crystallographer, and the chemist. It provides information concerning the behavior of atoms within the molecule and of the molecules themselves, which knowledge necessarily must be a prerequisite for the better understanding of the composition and behavior of all forms of matter.

NOTE.—No attempt has been made in the course of this presentation to recognize the contributions of individual workers, as the number of citations would be too numerous to be practicable. The reader is referred to the reviews by the author appearing in the Chemical Reviews **13**: 345. 1933 and **18**: 1. 1936 for most of the original citations.

MATHEMATICS.—*Population analysis: a theorem regarding the stable age distribution.*[1] ALFRED J. LOTKA, New York.

The author has elsewhere[2] stated without proof what amounts essentially to the theorem set forth below. As the proof is a little intricate it seems desirable to put it on record, as follows:

Theorem:—A closed population which is increasing at a constant rate r per head, under the régime of a constant age schedule of mortality and fertility, can have no other than the stable age distribution.

[1] Received May 18, 1937.
[2] Human Biology **9**: 104. 1937.

(That is, it can not be merely *approaching* that distribution, the stable distribution must be actually established.)

Concentrating attention exclusively on the female population, that is, dealing exclusively with mothers and daughters,[3]

Let $N(t)$, $b(t)$ and $d(t)$ denote, respectively, the number of the (female) population, its birth rate per head and its death rate per head at time t.

Let $p(a)$ be the probability at birth of reaching age a, and let $p'(a)$ denote the derivative $dp(a)/da$, these quantities being independent of t.

Let $m(a)$ be the frequency of female births by women at age a, independent of t.

It is to be noted that $p(a)$ and $m(a)$ from their nature can never be negative, while $p'(a)$ can never be positive.

Putting

$$B(t) = b(t)\ N(t) \tag{1}$$

and

$$D(t) = d(t)\ N(t) \tag{2}$$

we have the well known and essentially obvious relations

$$N(t) = \int_0^\infty B(t + a)p(a)da \tag{3}$$

$$B(t) = \int_0^\infty B(t - a)p(a)m(a)da \tag{4}$$

$$D(t) = -\int_0^\infty B(t - a)p'(a)da. \tag{5}$$

Hence

$$\frac{B(t) - D(t)}{N(t)} = \frac{\int_0^\infty B(t - a)\,[p(a)m(a) + p'(a)\,]da}{\int_0^\infty B(t - a)p(a)da} \tag{6}$$

$$= \text{constant (independent of } t) = r \tag{7}$$

by hypothesis, since this quotient is the rate of natural increase per head.

Two trivial cases may first of all be disposed of.

[3] As set forth in previous publications, e.g., Jour. American Statistical Association 20: 307, 329. 1925.

1. The condition (7) would be satisfied if

$$p(a)\, m(a) + p'(a) = \text{constant (independent of } a). \tag{8}$$

But this is contrary to biological facts.

2. The condition (7) is also satisfied if the numerator vanishes for all values of t. But in that case $r = 0$ and hence

$$N(t) = \int_0^\infty B(t - a)\, p(a)\, da = \text{constant} \tag{9}$$

that is,

$$B(t) = \text{constant} \tag{10}$$

and we have simply the case of a stationary population under the régime of a constant life table.

Furthermore the equation

$$B(t) = \int_0^\infty B(t - a)\, p(a)\, m(a)\, da \tag{4}$$

here becomes

$$1 = \int_0^\infty p(a)\, m(a)\, da \tag{11}$$

so that

$$r = 0 \tag{12}$$

satisfies the condition for stability of age distribution[4]

$$1 = \int_0^\infty e^{-ra}\, p(a)\, m(a)\, da. \tag{13}$$

3. There remains to be considered the general case, when the numerator of (6) does not vanish, and $r \neq 0$.

If, under these conditions, the quotient (6) is to be constant, $B(t-a)$ must be the product of a factor containing only t and a factor containing only a, that is, we must have

$$B(t - a) = Q\, F(t)\, f(a) \tag{14}$$

where Q is an arbitrary constant. We can so choose it that

$$f(0) = 1. \tag{15}$$

[4] A. J. LOTKA. Jour. American Statistical Association 20: 329. 1925.

Then

$$Q\,F(t) = B(t) \tag{16}$$

and

$$B(t - a) = B(t)\,f(a). \tag{17}$$

Furthermore

$$B(\overline{t - a_1} - a_2) = B(t - a_1)\,f(a_2) \tag{18}$$

that is

$$B(t - [a_1 + a_2]) = B(t)\,f(a_1)\,f(a_2) \tag{19}$$

$$= B(t)\,f(a_1 + a_2) \tag{20}$$

Hence

$$f(a_1 + a_2) = f(a_1)\,f(a_2), \tag{21}$$

and similarly

$$f(a + a + a + \cdots) = f(na) = [f(a)]^n \tag{22}$$

$$= [f(n)]^a \text{ by symmetry.} \tag{23}$$

Again,

$$f(1 \times a) = [f(1)]^a \tag{24}$$

But $f(1)$ is a constant. Let us put

$$f(1) = e^{-s} \tag{25}$$

where s is a constant still to be determined. Then, by (24)

$$f(a) = e^{-sa} \tag{26}$$

and by (17)

$$B(t - a) = B(t)\,e^{-sa} \tag{27}$$

that is, the births per unit of time increase in geometric progression at the rate s.

Furthermore, this is also the rate of natural increase per head of the population, for according to (5), (6) and (27) we have

$$\frac{B(t) - D(t)}{N(t)} = \frac{B(t) + B(t)\int_0^\infty e^{-sa}\,p'(a)\,da}{B(t)\int_0^\infty e^{-sa}\;p(a)\;da} \tag{28}$$

$$= \frac{1 - \{1 - s\int_0^\infty e^{-sa}\, p(a)\, da\}}{\int_0^\infty e^{-sa}\ p(a)\ da} \tag{29}$$

$$= s. \tag{30}$$

But by hypothesis this quotient is equal to the constant rate of increase r of the population. Hence

$$s = r. \tag{31}$$

Now, according to (4), (27) and (31)

$$B(t) = B(t)\int_0^\infty e^{-ra}\, p(a)\, m(a)\, da \tag{32}$$

$$1 = \int_0^\infty e^{-ra}\, p(a)\, m(a)\, da. \tag{33}$$

Therefore r is a root of (33). But r, the rate of natural increase, is constant by hypothesis. Therefore it must be a *real* root of (33), for complex roots would introduce oscillations. But (33) has only one real root, because $p(a)$, $m(a)$ is nowhere negative. If we denote this real root by ρ, we have therefore

$$r = \rho \tag{34}$$

and the coefficient of age distribution is given by

$$c(a) = \frac{B(t-a)}{N(t)}\, p(a) \tag{35}$$

$$= \frac{B(t)\, e^{-\rho a}}{N(t)}\, p(a) \tag{36}$$

$$= b\, e^{-\rho a}\, p(a). \tag{37}$$

But this is the stable age distribution. Thus, the conditions of the problem fully determine the age distribution (37) and none other is possible.

The theorem enunciated at the outset is therefore established.

BOTANY.—*New species of Costa Rican plants.*[1] C. V. MORTON, U. S. National Museum. (Communicated by WILLIAM R. MAXON.)

During the last two years the region about El General in the Province of San José, Costa Rica, has been intensively explored by Dr. Alexander F. Skutch. The flora has proved of great interest and the author plans to publish later a general discussion of its composition and relationships. The following new species represent only a portion of those thus far discovered by Dr. Skutch within this comparatively small area. It may be noted with pleasure that Professor Pax and Dr. K. Hoffmann have dedicated to him an interesting new genus of Euphorbiaceae.

Dioscorea borealis Morton, sp. nov.

Sect. *Centrostemon*. Herba dextrorsum volubilis; folia alterna longe petiolata, petiolo ca. 6 cm longo glabro sulcato; lamina foliorum late ovata, maxima 11.2 cm longa et 9.8 cm lata, apice acriter acuminata, basi leviter cordata, membranacea, utrinque concolor glabra integra, nervis primariis 9–11; inflorescentiae ♂ axillares, geminae vel ternae, usque ad 17 cm longae, non ramosae, rhachibus rectis subglabratis, floribus racemosis solitariis, numerosis, pedicellis 1–1.5 mm longis minute puberulis basi bracteatis, bracteis minutis subulatis puberulis; perianthii segmenta purpurea ovato-oblonga, 1.75 mm longa, patula, glabra; stamina 6, filamentis in tubum 1 mm longum connatis, antheris connatis sursum dehiscentibus; rudimentum stylinum nullum; flores ♀ ignoti.

Type in the U. S. National Herbarium, no. 1,638,052, collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 880 meters, June, 1936, by Alexander F. Skutch (no. 2638).

The only previously known North American species of the section *Centrostemon*, *D. panamensis* Knuth, is quite different from the present, which doubtless finds its closest relationship with *D. lareçajensis* Uline, of Bolivia, Peru, and Ecuador. Of this I have examined a specimen of the type collection (*Mandon* 1231) and find that the floral structure is essentially like that of *D. borealis*, but that the leaves are thicker, more prominently veined, and minutely puberulous on the nerves beneath. The leaves of *D. borealis* are perfectly glabrous.

Dioscorea remota Morton, sp. nov.

Sect. *Cryptantha*. Herba volubilis, caulibus dextrorsum scandentibus flavidis glabris striatis subangulatis; folia alterna longe petiolata, petiolo ca. 8.5 cm longo glabro paullo supra basin tumido; lamina foliorum late ovata, ca. 15 cm longa et 10.5 cm lata, integra, apice breviter (1.5 cm) acuminata, basi cordata, utrinque glabra, 7–9 nervia, nervis medianis areolam ovalem formantibus; inflorescentiae ♂ axillares, solitariae vel binae, perlongae, usque ad 90 cm longae, rhachi glabra non flexuosa,

[1] Published by permission of the Secretary of the Smithsonian Institution. Received March 1, 1937.

internodiis 1–6 cm distantibus, ramulis geminis simplicibus vel raro semel ramosis 4–11 cm longis, rhachibus interdum paullulum flexuosis basi bracteatis, bracteis lanceolatis ca. 5 mm longis; flores solitarii remoti sessiles bracteolati, bracteolis latis scariosis cucullatis concavis apiculatis glabris; perianthium purpureum glabrum, tubo cylindrico 2.75 mm longo, ca. 0.9 mm lato, lobis patulis ovatis 1.5 mm longis et 1 mm latis; stamina longe supra basin tubi perianthii inserta, filamentis alternatim inaequalibus, eis segmentis interioribus oppositis longioribus, ca. 1.2 mm longis, ceteris ca. 0.6 mm longis, antheris introrsis oblongis ca. 0.9 mm longis, ex fauce paullo exsertis; rudimentum stylinum nullum; flores ♀ ignoti.

Type in the U. S. National Herbarium, no. 1,642,272, collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 975 meters, December, 1935, by Alexander F. Skutch (no. 2197).

This, the first North American species of the section *Cryptantha*, need not be compared minutely with any of its Brazilian relatives, for it is well distinguished from all by its exceedingly long and relatively sparsely branched inflorescences, remote flowers, broad scarious bracteoles, and large flowers with elongate perianth tube, and by its large, ovate, deeply cordate leaves.

Costus formosus Morton, sp. nov.

Subg. *Eucostus*. Herba erecta caulescens 3.5 m alta; folia alterna, vagina brevi 4–5 cm longa inflata striata ubique brevissime puberulenta, ligula brevi usque ad 5 mm longa biloba margine longe ciliata; lamina foliorum sessilia oblanceolata vel oblonga, usque ad 23 cm longa et 7 cm lata vel verisimiliter majora, apice breviter acuminata, basi lata obtusa, supra glabra costa excepta, subtus ubique puberula; spica terminalis erecta sessilis cylindrica 19 cm longa et 4 cm lata, bracteis late ovatis obtusis dense imbricatis rubris (siccitate castaneis apice rubescentibus), ca. 4.7 cm longis, glabrescentibus, margine scariosis pilosulis, lineam dorsalem callosam flavam gerentibus; calyx ruber campanulatus glaber perspicue striatus, tubo 5 mm longo, 6 mm lato, lobis deltoideis ca. 5 mm longis margine scariosis pilosis; corollae tubus cylindricus 2–2.5 cm longus, 2.5–3.5 mm latus, flavus, lobis rubris oblanceolatis, ca. 4.3 cm. longis, 10–12 mm latis, glabris acutis; labellum flavum ca. 5.5 cm longum quam corolla brevius, glabrum, apice trilobum, lobis lateralibus ca. 6 mm longis et 5 mm latis apice leviter bilobulatis margine integris, lobo medio anguste lineari ca. 7 mm longo et 0.7 mm lato integro obtuso; stamen longissimum (ca. 7 cm longum), labellum et corollae lobos evidenter superans, filamento rubro petaloideo glabro 3–5 mm lato apice rotundato antheras 5 mm superante; ovarium 6–7 mm longum glabrum album; stylus gracilis glaber; stigma ca. 3.5 mm latum.

Type in the U. S. National Herbarium, no. 1,638,056, collected near El General, Prov. San José, Costa Rica, altitude 850 meters, July, 1936, by Alexander F. Skutch (no. 2775).

The most nearly related species is undoubtedly *Costus sanguineus* Donn. Sm., which agrees in corolla color, shape of bracts, and trilobed labellum, but nevertheless differs in many important characters, as follows:

Exterior corolla segment longer and broader than the remaining two, sericeous-pilose on the margins, about equaling the labellum; ovary densely pilose; middle lobe of the labellum shorter than the two lat-

eral lobes; filament produced above the anthers in a triangular acutish apex, this often inrolled; corolla tube over 5 mm. side; calyx sparsely sericeous; leaves densely long-hirsute on both surfaces; sheath long, tightly appressed, long-hirsute..... *C. sanguineus*

Exterior corolla segment equal to the others, glabrous, much exceeding the labellum; ovary glabrous; middle lobe of the labellum linear, exceeding the lateral lobes; filament produced above the anthers in a semi-orbicular plane apex; corolla tube slender, not over 3.5 mm. wide; calyx glabrous, except on the margins; leaves glabrous above, minutely puberulous beneath; sheath short, inflated, puberulous..... *C. formosus*

For definite determinations in *Costus* it is usually necessary to have flowers. Several non-flowering specimens from Costa Rica and Panama that have been identified as *C. sanguineus* are certainly not that species, and may belong to *C. formosus*, but I do not cite them because the leaf and sheath characters listed above may not hold when further collections are available.

Costus Skutchii Morton, sp. nov.

Subg. *Eucostus*. Herba caulescens; folia distincte sed breviter petiolata, petiolo glabro ca. 15 mm longo, vagina glabra longissima striata, ligula ca. 7 mm longa, aequaliter biloba haud truncata vel fissa, infra petiolum puberula, marginem versus pilosa; lamina foliorum oblongo-oblanceolata 25 cm longa et 7.2 cm lata (inferiores verisimiliter longiores), apice acriter acuminata, basi obtusa, supra glabra (nervo mediano excepto), subtus glabra; spica erecta ellipsoidea obtusa terminalis, 9 cm longa et 3.5 cm lata, bracteis rubris, siccitate nigrescentibus, dense imbricatis coriaceis, ca. 3.5 cm longis, apice rotundatis scariosis ciliatis non appendiculatis, linea callosa non perspicua, externe apicem versus glabratis inferne sericeopilosis, intus glabris; calyx tubulosus 7 mm longus, coriaceus sericeus, leviter trilobatus; corollae tubus flavus ca. 2 cm longus, anguste cylindricus, lobis anguste obovatis coccineis, ca. 3 cm longis et 1.2 cm latis, integris glabris, apice rotundatis; labellum corolla longius, ca. 7 cm longum, cucullatum, rubro-purpureum, venis pallidis, non lobatum, apice ca. 4.5 cm latum subtruncatum perspicue lacerato-dentatum, basin versus squamiferum; ovarium cylindricum ca. 4.5 mm longum, glabrum.

Type in the U. S. National Herbarium, no. 1,638,054, collected near El General, Prov. San José, Costa Rica, altitude 850 meters, July, 1936, by Alexander F. Skutch (no. 2690).

The most nearly related species is probably *Costus cylindricus* Jacq., which has yellow corollas, with the tube only 1 cm long, and a smaller, yellow, entire labellum. *Costus spicatus* L. differs in its smaller, yellow, differently formed flowers, as well as in other characters. The corolla lobes of *C. sanguineus* Donn. Sm. are similar in color to those of the present species, but the labellum is entirely different in color, size, and shape. *Costus splendens* Donn. Sm. differs widely in the shape of the labellum, as well as in other characters.

Skutchia Pax & K. Hoffm., gen. nov.

Flores dioici, ♂ apetali, ♀ nudi. Sepala ♂4, ad medium fere connata, imbricata. Stamina 4, episepala; filamenta libera, sepalis longiore, in ala-

bastro incurva; antherae biloculares, introrsae. Discus O. Ovarii rudimentum columnare. Ovarium biloculare, loculo uno abortivo; styli 2, fere liberi, papillosi; ovulum solitarium, pendulum.—Arbor, partibus juvenilibus et inflorescentiis exceptis, glabra. Folia alterna, petiolata, penninervia; stipulae deciduae. Inflorescentiae axillares, satis longae, ♂ amentiformes, squamis parvis, triangularibus, juxta vel interflores sitis onustae. Flores ♂ sessiles, ♀ pedicellati. Fructus ignotus.

Skutchia caudata Pax & K. Hoffm., sp. nov.

Arbor, ca. 18 m alta. Ramuli graciles, juveniles compressi breviter puberuli; rami teretes, glabri, striati, cortice rubro-brunneo tecti. Petiolus ca. 1 cm longus; limbus 10–12 cm longus, 3–3.8 cm latus, lanceolatus, leviter falcatus, caudato-acuminatus, basi acutus, integer, chartaceus, eglandulosus, reticulato-venosus; costae secundariae ca. 8, arcuato-adscendentes, prope marginem anastomosantes; stipulae ca. 1 mm longae, triangulares, breviter acuminatae. Inflorescentiae ♂ ca. 8 cm longae, satis densiflorae, ♀ ca. 10 cm longae, pendulae, utriusque sexus breviter puberulae et glandulis parvis adspersae. Flores ♂ ca. 2 mm lati. Calycis ♂ lobi ovati, acuti, basi subsaccati, extus parce pilosi, apice fimbriati. Filamenta ca. 3 mm longa, calyce duplo longiora. Ovarii rudimentum calyce brevius, pilosum. Pedicelli ♀ 1–3 mm longi. Ovarium verrucosum; styli ad 3 mm longi.

Type in the U. S. National Herbarium, no. 1,641,605, a pistillate plant collected near El General, Prov. San José, Costa Rica, altitude 950 meters, January, 1936, by Alexander F. Skutch (no. 2383). The staminate specimen collected at the same time and place is no. 2386.

"Mr. C. V. Morton, who is working on the Skutch collection, has already recognized that these specimens represent a new genus, which he believes related to *Tetrorchidium*. *Skutchia* belongs, to be sure, to the Gelonieae, but is nevertheless tolerably isolated in the group and is not more nearly related to *Tetrorchidium* than to other genera of this tribe. It is distinguished from all other Gelonieae by the naked pistillate flowers and by the ovary being one-celled through abortion of the second cell. Furthermore the inflexed stamens are remarkable."

Heliocarpus excelsior Morton, sp. nov.

Arbor altissima, 36 m alta, ramuli teretes stellato-puberulenti lenticellis conspicuis praediti; folia alterna stipulata (stipulis deciduis), petiolata, petiolo tereti usque ad 12 cm longo stellato-puberulento; lamina foliorum usque ad 19 cm longa et 18 cm lata, apicem versus sinuato-triloba lobo terminali et lobis lateralibus acuminatis, basi leviter cordata, appendiculata, appendiculis ca. 4, glanduliferis, membranacea serrulata utrinque concolor minute stellato-puberulenta, nervis 7 primariis digitatis; inflorescentia magna terminalis, 15 cm alta et 23 cm lata, rhachibus stellato puberulentis, pedicellis gracilibus usque ad 8 mm longis; alabastra obovata ca. 4.5 mm longa; sepala oblonga 6 mm longa, ca. 1.6 mm lata, acuta exappendiculata externe puberulenta; petala sepalis breviora spathulata ca. 4 mm longa glabra plerumque leviter crispa; stamina 16–19; stylus 2 mm longus, breviter bifidus, ovario longior; capsula cum radiis 6–8 mm lata, stipitata (5 mm), corpore capsulae anguste elliptico, 4 mm longo, 1.6 mm lato, dense piloso, radiis ca. 4 mm longis, longe pilosis.

Type in the U. S. National Herbarium, no. 1,642,302, a fruiting specimen

collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 1100 meters, December, 1935, by Alexander F. Skutch (no. 2250). The flowers are described from *Skutch* 2266, collected near the same locality at an altitude of 825 meters.

The only related species are *Heliocarpus appendiculatus* Turcz. and *H. chontalensis* Sprague, both of which may be at once distinguished by their conspicuously discolorous leaves with a conspicuous, dense, whitish or yellowish tomentum beneath. The leaves of *H. excelsior* are concolorous and the hairs are minute, sparse, and scarcely visible except under a lens. The leaves of *H. excelsior* differ in shape also, being almost square in outline, with cordate base, trilobate apex, and lightly serrulate margins; on the contrary those of *H. appendiculatus* and *H. chontalensis* are ovate, usually unlobed and in *H. appendiculatus* coarsely serrate. Other differences are also apparent, such as the narrower capsule body, the fewer stamens, and the differently shaped leaf appendages. *Heliocarpus excelsior* is the largest known tree of the genus.

Begonia lignescens Morton, sp. nov.

Sect. *Ruizopavonia*? Caules elongati scandentes lignosi glabri, nodis incrassatis radicantes; folia alterna stipulata, stipulis caducis, cicatricibus perspicuis, petiolata, petiolo brevi ca. 3 mm longo fuscescente glabro; lamina foliorum anguste oblonga, 7–9 cm longa et 2–2.6 cm lata, obliqua, apice breviter acuminata, basi cuneata obliqua, membranacea apicem versus paullo denticulata utrinque glabra non squamosa, pennivenia, venis primariis 4–5-jugis subtus fuscescentibus; inflorescentiae monoicae terminales usque ad 16 cm longae et 20 cm latae, pedunculatae (pedunculo 3.5–4 cm longo), cymosae, multoties dichotomae, rhachibus glabris leviter angulatis, bracteis caducis longe lanceolatis acutis glabris; sepala floris ♂ duo alba lancolata, 15 mm longa et 5 mm lata, acuta glabra; petala 2 minuta ca. 2.5 mm longa; stamina numerosa, filamentis liberis quam antheris multo brevioribus; sepala floris ♀ alba duo elongato-lanceolata, fere 2 cm longa et 5 mm lata, glabra acuta; petala nulla; ovarium glabrum triloculatum trialatum, ala una (immatura) 1 cm longa cultriformi, alis ceteris reductis minimis, placentis bilamellatis ubique ovuliferis; styli tres basi connati sursum abrupte expansi bifidi, ramis spiraliter contortis ubique papillosis.

Type in the U. S. National Herbarium, no. 1,638,058–9, collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 1160 meters, August, 1936, by Alexander F. Skutch (no. 2853).

Although similar in leaves and habit to *Begonia estrellensis* C. DC., the large acute narrowly lanceolate sepals of *B. lignescens* are distinctive and like no other species of the genus that I know. The sepals of *B. estrellensis* are small, rounded, and orbicular. These two species seem to be most naturally placed in the section *Ruizopavonia*, as characterized by Irmscher, from which they differ, however, in having male flowers with petals.

Cavendishia Skutchii A. C. Smith, sp. nov.

Frutex epiphyticus; ramulis subteretibus glabris rugosis; petiolis glabris rugosis 5–10 mm longis; laminis tenuiter coriaceis, in sicco metallico-sub-

caeruleis, oblongis, 10–15 cm longis, 3.5–5 cm latis, basi subcordatis vel subtruncatis, apice obtusis vel breviter et obtuse acuminatis, margine leviter incrassatis, supra glabris nitidis, subtus parce brunneo-pilosis vel punctatis, 5-pli-nerviis, nervis prope basin orientibus, supra impressis (vel inferioribus elevatis), subtus prominentibus, venulis utrinque prominulis; inflorescentiis axillaribus aliquot ad apices ramulorum, racemosis, 15–20-floris, subglabris, basi bracteis deciduis instructis; rhachide 5–7 cm longa; floribus in axillis bractearum alternarum solitariis, bracteis membranaceis integris oblongis vel late ovatis, 18–23 mm longis, 12–15 mm latis; pedicellis subteretibus 6–12 mm longis, basi et apice incrassatis, prope basin bibracteolatis, bracteolis membranaceis oblongis, 3–4 mm longis, margine sparse fimbriatis; calyce coriaceo, 4–5 mm longo et diametro, limbo suberecto tubum subaequante, lobis 5 deltoideis 1–1.5 mm longis acutis, margine breviter glanduloso-fimbriatis; corolla membranacea vel tenuiter carnosa, cylindrica, basi et apice alba, medio rosea, maturitate 13–15 mm longa, 3–4 mm diametro, apice contracta, lobis 5 parvis subacutis; staminibus subaequalibus, filamentis ligulatis tenuiter carnosis, superne intus breviter pilosis, alternatim 2 mm et 5 mm longis, connectivis nigrescentibus carnosis, antheris membranaceis flavis, alternatim 12 mm et 10 mm longis, tubulis amplis quam loculis 3-plo longioribus, per rimas elongatas dehiscentibus; stylo corollam subaequante, stigmate capitato.

Type in the U. S. National Herbarium, no. 1,642,549, collected in forest in the vicinity of El General, Province of San José, Costa Rica, at 1100 meters altitude, in August, 1936, by A. F. Skutch (no. 2802).

The closest ally of the new species appears to be *C. crassifolia* (Benth.) Hemsl., of southern Mexico and Guatemala. The present species differs from that by its slightly larger and metallic-colored leaves, which are usually subcordate rather than cuneate at base. In floral characters the two species are very similar; *C. Skutchii* has larger bractlets of the pedicels and has the calyx glabrous rather than brown-pilose distally.

Ardisia Skutchii Morton, sp. nov.

Subg. *Graphardisia*. Frutex 7.5 m altus; ramuli subteretes ca. 3.5 mm diam. glabri leviter striati; folia alterna estipulata, subsessilia, lamina oblanceolata usque ad 26 cm longa et 7 cm lata, apice acuminata, basi longe attenuata, papyracea integra utrinque pallidi concolori glabra eglanduliferi, venis primariis ca. 12-jugis arcuatis; inflorescentia alba terminalis ca. 10 cm longa et 12 cm lata, brevissime pedunculata bracteis magnis obovatis ca. 25 mm longis suffulta, rhachibus plus minus flexuosis robustis glabris eglanduliferis, inflorescentiis ultimis corymbosis paucifloris bracteis oblongis vel obovatis magnis suffultis, pedicellis 12–15 mm longis gracilibus glabris apice incrassatis; sepala alba imbricata late ovata, ca. 5.5 mm longa et 4 mm lata, rotundata glabra punctis lineatis satis paucis perspicuis picta; corolla alba roseo-tincta, ca. 15 mm lata, rotata, tubo ca. 2 mm longo, lobis late ovatis ca. 7 mm longis, 5 mm latis, obtusis glabris punctis dissite pictis; filamenta ca. 2 mm longa, crassa eglandulifera, basin versus latioribus et in tubum brevem connata; antherae lanceolatae 3 mm longae, non exsertae, poris apicalibus dehiscentes; ovarium glabrum conicum; stylus gracilis 4.5 mm longus glaber.

Type in the U. S. National Herbarium, no. 1,638,053, collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 1070 meters, June, 1936, by Alexander F. Skutch (no. 2660).

The only related species is *Ardisia opegrapha* Oerst., which differs as follows:

Sepals oblong, 6 mm long, 2–3 mm wide; filaments and filament tube glanduliferous ..... *A. opegrapha*

Sepals broadly ovate, 5.5 mm long, 4 mm wide; filaments and filament tube eglanduliferous ..... *A. Skutchii*

Other differences also exist. The leaves of *A. opegrapha* are obviously petiolate, but those of *A. Skutchii* are almost sessile. The entire inflorescence of *A. opegrapha* is said by Mez to be deep rose and is so figured by Hooker (Bot. Mag. *pl. 6357*); that of *A. Skutchii* is, according to the collector, entirely white except for a faint pink tinge on the corolla.

Leiphamos lutea Morton, sp. nov.

Herba parasitica alba vel flavescens; caules 10–20 cm alti, ca. 1 mm lati, glabri teretes uniflori, bracteis 7–16-jugis lanceolatis ca. 6.5 mm longis, interdum apice unidenticulatis, basi fere ad medium connatis; pedunculus subnullus, vix 2 mm longus; calycis tubus ebracteatus 5 mm longus corollae arcte appressus, lobis 5 lanceolatis 2.75 mm longis, 1 mm basi latis, integris, acutis; corolla hypocrateriformis, tubo flavo 3.2–3.6 cm longo, basi et apice inflato, medio cylindrico, ca. 2 mm lato, glabro, fauce intus papilloso, lobis luteis late ovatis 6–9 mm longis, obliquis glabris cuspidatis patentibus; antherae sessiles exappendiculatae liberae faucem versus insertae; ovarium substipitatum ca. 13 mm longum glabrum eglanduliferum; stylus inclusus glaber ca. 15 mm longus; stigma compressum.

Type in the U. S. National Herbarium, no. 1,638,055, collected near El General, Prov. San José, Costa Rica, altitude 1130 meters, July, 1936, by Alexander F. Skutch (no. 2767).

Leiphamos aphylla (Jacq.) Gilg of the West Indies and South America is closely related but may be distinguished by its narrower, obtuse or merely acute corolla lobes; those of the present species are abruptly cuspidate-acuminate. *Leiphamos costaricensis* Standl. differs in its corolla lobes, as well as in its stamens. Another recent segregate from *L. aphylla* is *L. eximia* Sandw. of British Guiana, which also differs from *L. lutea* in its anthers and corolla lobes.

Columnea florida Morton, sp. nov.

Subg. *Collandra*. Frutex epiphyticus; caules crassi ca. 1 cm diam., pallidi vel rubescentes purpureo-maculati perspicue sulcati, hornotini hirsuti, pilis flaccidis multiseptatis, annotini glabrescentes; folia opposita valde inaequalia, majora breviter petiolata, petiolo 1 cm longo crasso densissime hirsuto; lamina foliorum majorum oblanceolata, maxima 35.5 cm longa et 10.5 cm lata, siccitate chartacea vel subcoriacea, apice breviter et acriter acuminata (ca. 2 cm), basi obtusa obliqua, margine integra, supra glabra vel basin versus pilis perpaucis instructa, apicem versus maculas 2 rubras gerens, subtus pallidior, apicem versus perspicue rubro-maculata, ubique appresso-pilosa, costa basi hirsuta, venis primariis ca. 12-jugis arcuatis; lamina foliorum minorum subsessilia anguste elliptica, ca. 3 cm longa, longe acuminata, supra glabra, subtus dense pilosa, venis paucis obscuris; flores axillares, in ramulis annotinis defoliatis et in hornotinis fasciculati, pauci vel

plures, pedicellis crassis usque ad 1 cm longis, dense hirsutis, medio bracteatis, bracteis parvis lanceolatis dense hirsutis; calycis lobi 5 liberi, ambitu ovati, 2.3 cm longi, ca. 1 cm lati, utrinque densissime hirsuti, pectinato-incisi, dentibus numerosis anguste linearibus viridibus viridi-hirsutis corolla crassa flava (*fide* Skutch), ca. 25 mm longa, 9 mm lata, tubo cylindrico vix ventricoso externe densissime brunneo-hirsuto, intus sparse puberulo, fauce paullo contracto, limbo vix 5 mm lato, lobis parvis erectis suborbiculatis ca. 2.5 mm longis et 3 mm latis crassis glabratis; filamenta basi in tubum liberum postice fissum 5 mm altum connata, partibus liberis pilosulis contortis; antherae per paria leviter connatae, connectivo oblongo crasso, loculis contiguis oblongis discretis 3 mm longis glabris; discus ad glandulam dorsalem magnam crassam 1.5 mm altam 3.5 mm latam leviter trilobatam glabram reductus; ovarium conicum dense pilosum; stylus 12 mm longus pilosulus; stigma leviter bilobum; bacca globosa, ca. 12 mm diam., pericarpio coriaceo; placentae lamellae intus solum ovuliferae; semina rubra fusiformia, ca. 1.2 mm longa, 0.5 mm lata striata, striis leviter et spiraliter contortis.

Type in the U. S. National Herbarium, no. 1,642,394, collected in the vicinity of El General, Prov. San José, Costa Rica, altitude 915 meters, January, 1936, by Alexander F. Skutch (no. 2436). Additional specimens referable to this species are:

COSTA RICA: Type locality, January, 1891, *Pittier* 4020. Cañas Gordas, alt. 1100 meters, February, 1897, *Pittier* 11198.

PANAMA: Cerro de Garagará, Sambú Basin, southern Darien, alt. 500–974 meters, Feb. 7, 1912, *Pittier* 5664.

All these older specimens have been previously identified as *Columnea sanguinea* Hanst., but this West Indian species differs widely in its thinner, toothed leaves, these pilose above, in its differently shaped, fewer-toothed calyx lobes, and in several other important points. The related Costa Rican species, *C. consanguinea* Hanst. and *C. purpurata* Hanst., differ also in both leaves and flowers. The above description of the fruit and seeds is drawn from *Pittier* 5664.

Drymonia fimbriata Morton, sp. nov.

Frute 1.5 m altus; caules argute quadrangulati, hornotini minute strigillosi, annotini glabrescentes pustulati; folia opposita aequalia petiolata, petiolo usque ad 4.7 cm longo, strigilloso pustulato vel transverse corrugato, lamina foliorum late ovata 22 cm longa et 11 cm lata, obliqua, apice breviter acuminata, basi obliqua in petiolum longe decurrens, supra viridis fere glabra pilis paucis antrorsis appressis subsetulosis adspersa, subtus pallida in mesophyllo parcissime strigillosa, costa et venis pustulatis strigillosis, margine denticulata, venis primariis 6 vel 7-jugis; flores in axillis defoliatis aggregati numerosi, pedunculo communi nullo, pedicellis ca. 13 mm longis strigillosis apicem versus sulcatis basi bracteatis, bracteis lanceolatis integris puberulis ca. 5 mm longis, calycis lobi oblongi subaequales liberi, ca. 15 mm longi, 6 mm lati, accrescentes tum 20 mm longi et 9 mm lati, utrinque puberuli, longe pectinato-fimbriati, dentibus filiformibus puberulis inaequalibus usque ad 10 mm longis basi saepe furcatis; corolla alba basi longe calcarata (4.5 mm), tubo externe ubique pilosulo obliquo ca. 28 mm longo, basi 2.5 mm lato, sursum inflato fauce non contracto 10–12 mm lato, limbo rubro-venoso glabro obliquo bilabiato, lobo inferiore flabelliformi 11 mm longo apice 22 mm lato lacerato-dentato, lobis lateralibus integris late deltoideis 9 mm longis et

11 mm latis, lobis superioribus minoribus subrotundis 8 mm longis apice eroso-laceratis; filamenta in tubum 14 mm longum liberum postice fissum connata, partibus liberis glabris non contortis; antherae oblongae connatae; discus in glandulam posticam glabram 1.5 mm longam 3 mm latam reductus; ovarium conicum puberulum; stylus brevis crassus glaber ca. 12 mm longus; stigma latum bilobum; placentarum lamellae intus solum ovuliferae.

Type in the U. S. National Herbarium, no. 1,638,057, collected near El General, Prov. San José, Costa Rica, altitude 880 meters, August, 1936, by Alexander F. Skutch (no. 2839).

The filiform-pectinate calyx lobes of this species are unique in the genus *Drymonia*.

ZOOLOGY.—*A necessary change in an amphibian name.*[1] DORIS M. COCHRAN, U. S. National Museum. (Communicated by ROLAND W. BROWN.)

In 1935[2] I described some new species of frogs collected by P. J. Darlington in the La Selle Range of southwestern Haiti. It now appears that the frog which I named *Leptodactylus darlingtoni* (p. 372) is in reality an *Eleutherodactylus* with very narrow T-shaped terminal phalanges even though in the form of its digits it is a distinct approach to *Leptodactylus*. Dr. E. R. Dunn has pointed out this structural feature, and Dr. G. K. Noble has confirmed it. As I had already named a different frog from the same locality *Eleutherodactylus darlingtoni* on pl. 368 of the same publication, it becomes necessary to change the name of *Leptodactylus darlingtoni* Cochran. I therefore propose the name *Eleutherodactylus jugans* to take the place of *Leptodactylus darlingtoni* Cochran.

ENTOMOLOGY.—*Notes on Curculionidae (Coleoptera).*[1] L. L. BUCHANAN, Bureau of Entomology and Plant Quarantine. (Communicated by C. F. W. MUESEBECK.)

Most of the following notes are here put on record as a basis for the use of certain names in forthcoming papers.

Trachyphloeus bifoveolatus Beck

Trachyphloeus bifoveolatus Beck 1817, Beitrage zur baierischen Insecten Fauna, p. 22.

The U. S. National Museum collection contains specimens of this European species from New York (Barneveld, 1917, and Oriskany, 1931); Nova Scotia (Riverport, 1936); New Brunswick (Chipman, 1936). The New York specimens previously were identified as *T. davisi* Blatchley, a species de-

[1] Received April 29, 1937.
[2] Boston Soc. Nat. Hist. Proc. 40 (6): 367–376. 1935.
[1] Received March 17, 1937.

scribed from Staten Island, N. Y., in 1916 (Rhynchophora of Northeastern America, p. 115). Blatchley's species evidently is closely related to *bifoveolatus*, but differs, by description, in having only 2 spines at the apex of the front tibia (3 or 4 distinct spines, and often 2 or more shorter ones, in *bifoveolatus*), and presumably in lacking the pronotal foveae which are usually well developed, though sometimes encrusted, in *bifoveolatus*. *T. asperatus* Boh. 1843 (Genera et Species Curculionidum, VII, 1, p. 116) described from "America borealis ad Boston," remains unrecognized.

GYMNAETRON Schoenherr

Three species of this genus, all of European origin, are now known from North America. In the males of all three the tibiae are mucronate, the mucro of each tibia projecting at a right, or slightly obtuse, angle. In the females the front and middle tibiae are mucronate about as in the males; but the hind tibia is unarmed in *teter*, or armed in *netum* with a black spine which differs from the male mucro in being more slender and in being porrect or subporrect. In *antirrhini* the female hind tibia is virtually unarmed, although a minute spine is present in some specimens. The derm is black in all three species but in *teter* and *netum* the vestiture is paler, somewhat coarser, and more generally prostrate, and covers a greater proportion of the surface, resulting in a lighter ground color; whereas in the blackish appearing *antirrhini* the vestiture, besides being darker, is somewhat finer, and (at least on pronotum) more generally erect, thus leaving exposed a greater proportion of the dermal surface. In the following summaries the two varieties of *teter*—*subrotundatum* Reitter and *plagiellum* Gyll.—are not distinguished, the former apparently being no more than a depauperate form, the latter including specimens having the elytra more or less extensively dull reddish apically. The rostral length is the shortest distance between the apex of the rostrum and the front margin of the eye at its middle.

SUMMARIES OF DIFFERENTIAL CHARACTERS

1. Average length about 2.5 mm (extremes, 2.2–3 mm); ground color blackish; rostrum two-thirds to three-fourths as long as pronotum, rather strongly tapering in dorsal view from antennal socket to apex; rostrum in side view thick at base, tapering throughout, apical half (especially in male) more strongly tapering; prothorax about three-fourths as long as wide; scutellum about as long as wide; elytral striae half to two-thirds as wide as the intervals, the intervals flat and irregularly, biseriately punctate; femora similar in the sexes, of normal size, each with a minute tooth. Massachusetts, Connecticut, New York, New Jersey. Reared from seed pods of *Linaria vulgaris* by P. H. Timberlake and by D. H. Blake ..... *antirrhini* Paykull

   Length usually 2.7 mm or more; ground color brownish to gray; rostrum longer, often virtually as long as pronotum; prothorax about two-thirds as long as wide; elytral striae narrower, the intervals relatively much wider and normally with 3 very irregular rows of punctures (2 rows in some of the very small specimens). 2

2. Average length between 2.7 and 3.2 mm (extremes 2–3.5 mm); rostrum five-sixths to nearly as long as pronotum (longer in females); scutellum about as long as wide; femora not dilated, of subequal size in the sexes, each femur with a small to moderate sized tooth. ♂: No fringe on lower edge of hind tibia; rostrum, in dorsal view, very feebly tapering from antennal socket to apex. ♀: Rostrum slightly but obviously arcuate, apical half cylindrical, polished, and sparsely punctulate (often appearing smooth). Connecticut, New York, New Jersey, Pennsylvania, Virginia, Iowa. Reared from *Linaria vulgaris* by J. C. Bridwell and by A. B. Champlain.....*netum* Germar

Average length between 3.2 and 4 mm (extremes, 2.5–4.25 mm); rostrum averaging a little longer, often virtually as long as pronotum in female and only a trifle shorter in male; scutellum distinctly, usually much, wider than long. ♂: Femora dilated and strongly toothed (especially front pair); lower edge of hind tibia fringed with long, suberect hair in apical half; rostrum, in dorsal view, more distinctly tapering apically. ♀: Rostrum straight or nearly so, distinctly tapering from base to apex in side view, apical half rather strongly, not densely, punctate. Generally distributed east of the Mississippi River from southern Canada to Georgia; west of the Mississippi, specimens are at hand from Minnesota, Iowa, Missouri, Kansas, Oklahoma, Texas, Colorado, Washington, Oregon. On mullein.....*teter* Fabricius

Ceutorhynchus punctiger Gyllenhal

Ceutorhynchus punctiger Gyllenhal (*C. marginatus* of American authors, not Paykull).

This European species seems to be established in North America. Specimens in the Museum collection are from Ontario, Quebec, Massachusetts, New York, New Jersey, Pennsylvania, Michigan, Indiana.

Perigaster lituratus (Dietz), n. comb.

Coelogaster lituratus Dietz 1896, Trans. Amer. Ent. Soc. **23**: 457.
Perigaster longirostris Buchanan 1931, Jour. Wash. Acad. Sci. **21**: 323 (new synonymy).

Dietz did not describe the minutely toothed tarsal claws and the obsolescent antennal scrobe of *lituratus*, important characters in which it differs from *zimmermanni* Gyll., the genotype of (*Coelogaster*) = *Dietzella*. In *zimmermanni* the claws are strongly toothed and the scrobe is deep and complete. Although *lituratus* has an ocular lobe, a structure not found in the other species of *Perigaster*, its characters in general place it with *Perigaster* and not with *Dietzella*. *P. lituratus* is known from Ontario, New York, New Jersey, Michigan, Illinois, Iowa, Washington.

PHYTOBIUS Schoenherr, and allied genera

Different interpretations of *Phytobius* and allied genera have resulted in considerable confusion, and, at least in North America, misidentifications and omissions have further clouded published records. The data here assembled, though incomplete, tend to harmonize contradictions in the nomenclature.

Schoenherr erected *Phytobius* (evidently a Schmidt manuscript name) in 1836, citing in its synonymy *Hydaticus* Schoenherr 1826 (preoccupied by *Hydaticus* Leach 1817 in Dytiscidae). In his 1826 description of *Hydaticus* Schoenherr designated *velatus* Beck as type, but in his 1836 description of *Phytobius* he failed to set a type although it is obvious from the context that he intended *Phytobius* primarily as a substitute genus for *Hydaticus*, and that he intended *velatus*, the type of *Hydaticus*, to "carry over" and become the type of *Phytobius*. However, because *Hydaticus* 1826 and *Phytobius* 1836 are not co-extensive, and because Schoenherr did not set a type for *Phytobius* in unequivocal terms, it seems necessary to accept C. G. Thomson's 1859 type designations in *Phytobius*, *Pelenomus*, *Eubrychius*, and *Litodactylus*. On this basis, the American genera and species take the following arrangement:

PHYTOBIUS Schoenherr

Phytobius Schoenherr 1836, Gen. et Sp. Curc., III, 1, p. 458; genotype, *4-tuberculatus* F., designated by Thomson 1859, Skandinaviens Coleoptera, I, p. 138.

Pelenomus Thoms., ibid.; genotype, *comari* Hbst., designated by Thomson, ibid.

Phytobius thus becomes the valid generic name for the American species *cavifrons* Lec. to *pusillus* Dtz., inclusive, now listed in the Leng catalogue under *Pelenomus*.

EUBRYCHIUS Thomson

Eubrychius Thomson 1859, ibid., p. 138; genotype (*aquaticus* Thoms.) = *velatus* Beck, designated by Thomson, ibid.

Includes only the genotype species, which is apparently confined to Europe, though wrongly recorded from North America. The American species concerned is *Eubrychiopsis lecontei* Dtz. (See below.)

LITODACTYLUS Redtenbacker

Litodactylus Redtenbacker 1849, Fauna Austriaca, I, p. 399; genotype (*myriophylli* Gyll.) = *leucogaster* Marsham, designated by Thomson 1859, Skand. Coleop., I, p. 138.

Includes 1 American species, *griseomicans* Schwarz (*griseomicans* Dtz.) which is closely related to the European *L. leucogaster* Marsh. Specimens of *griseomicans* are at hand from Dane County, Wisconsin; Okoboji, Iowa; Wahpeton, North Dakota; Kansas; Richfield, Utah; Kahlotus, Washington; Medicine Hat, Alberta. Schwarz lists two localities (Kansas and Dakota) in the original description. The type specimen, now in the National Museum, is labeled "Ks" (Kansas).

EUBRYCHIOPSIS Dietz

Eubrychiopsis Dietz 1896, Trans. Amer. Ent. Soc., v. 23, p. 474; monobasic genotype, *E. lecontei* Dtz. (*Phytobius velatus* of American authors, not *Eubrychius velatus* Beck).

As far as known, *Eubrychiopsis* includes only the 2 American species, *lecontei* Dtz. and *albertanus* Brown. Specimens of *lecontei* in the National Museum are from Detroit, Michigan (type locality); Dane County and Madison, Wisconsin; Lake Okoboji, Iowa. The Massachusetts and Vancouver localities mentioned by Blatchley and Leng 1916, p. 464, may not refer to this species. Dietz's original description of *lecontei* calls for 2 small cusps on the anterior margin of the prothorax; but Dr. Darlington has examined Dietz's type and found no such cusps present, nor are they present on any of the specimens in the Museum collection. Specimens of *albertanus* in the Museum are from Creston, British Columbia, and Last Mt. Lake, Saskatchewan. The type locality is Waterton Lakes, Alberta.

For key to the 3 American species discussed above, see Brown, Can. Ent., vol. 64, 1932, pp. 10–12.

Conotrachelus Schoenherr

Conotrachelus Schoenherr 1837, Gen. et Sp. Curc., IV, 1, p. 392.
Loceptes Casey 1910, Can. Ent. **42**: 130 (new synonymy).

Conotrachelus recessus (Casey), n. comb.

Loceptes recessus Casey 1910, Can. Ent. **42**: 130.
Conotrachelus atokanus Fall 1913, Trans. Amer. Ent. Soc. **39**: 65 (new synonymy).

Casey placed *Loceptes* in the Tychiini, although the monobasic genotype, *recessus* Csy., clearly belongs in *Conotrachelus*. Mr. Fall has compared specimens of *recessus* Csy. with the type of *atokanus* Fall and has verified the species' synonymy recorded above. Examples of *C. recessus* in the Museum are from Atoka, Oklahoma (type locality); Douglas County, Kansas; Aberfoyle, Bonham, Clarksville, Greenville, and Dallas, Texas. Mr. Fall has specimens from Oklahoma and Arkansas (Hope).